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INSTRUCTION

IN

CHEMICAL ANALYSIS.

(Qualitative.)

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INSTRUCTION

IN

CHEMICAL ANALYSIS.

(Qualitative.)

BY

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WITH

A PREFACE BY PROFESSOR LIEBIG.

EDITED BY

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MEMBER OF THE CHEMICAL SOCIETY, LATE OF THE GIESSEN AND PARIS
LABORATORIES.

SECOND EDITION.

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EDITOR'S PREFACE

TO THE

SECOND EDITION.

The rapid sale of the first English Edition of this Work has justified the anticipation of the illustrious Chemist, at whose suggestion I undertook to place it at the service of the English student of chemistry. The numerous commendations it received from the press, I may be allowed to say, in my capacity of Editor, it fully deserves. The present edition is almost a new work, so numerous and important are the additions and alterations which are so incorporated into its structure that they could not be produced separately. It represents the Fourth German edition. Several new works on the same subject, of various pretensions, have made their appearance in this country since this was published—they have not retarded, on the contrary they seem rather to have facilitated its sale.

The increasing taste for practical chemistry, indicated by this efflux of books, calls especially for works detailing methods which may be safely followed and implicitly relied on. I venture to affirm, that in this respect, the work of Dr. Fresenius is pre-eminent. Moreover, those works intended particularly for the use of students who enjoy the advantage of tuition in a laboratory, omit many things which it is absolutely necessary for him to know from some source. Indeed this is the only work in the English language adapted for self-instruction. With a previous general acquaintance with chemistry, derived from attendance on a course of lectures, or from the perusal of some introduction to the science of which many excellent ones exist, any person may take up this work, and make himself an expert analyst. And after all the assistance given by a teacher, the chemist, when left to his own resources, still requires a guide to whom he may safely have recourse for facts which have escaped his memory. Both as a systematic course of study, and as a book of reference, Dr. Fresenius's work is unrivalled. It has been duly appreciated, since it is now translated into most European languages, and reprinted in America.

J. LLOYD BULLOCK.

22, *Conduit Street, May*, 1846.

PREFACE

BY PROFESSOR LIEBIG.

Dr. Fresenius conducts the course of elementary instruction, in mineral analysis, in the laboratory of the University of Giessen. During the two last sessions he has followed the method described in his work, entitled, "Elementary Instruction in Qualitative Chemical Analysis." This method I can confidently recommend from my own personal experience to all who are desirous of obtaining instructions in inorganic analysis, for its simplicity, usefulness, and the facility with which it may be apprehended.

I consider Dr. Fresenius' work extremely useful as an introduction to Professor H. Rose's excellent manual, and for adoption in institutions where practical chemistry is taught, but it is especially adapted to the use of Pharmaceutical Chemists.

Further, a number of experiments and discoveries have been recently made in our laboratory, which have enabled Dr. Fresenius to give many new and simplified methods of separating substances, which will render his work equally welcome to those who already are familiar with the larger works on inorganic analysis.

JUSTUS LIEBIG.

EDITOR'S PREFACE.

This work of Dr. Fresenius has already gone through two editions in Germany. The abundant opportunities enjoyed by its author of discovering the wants felt by students in entering upon the practice of chemical analysis, and his position in the school at Giessen, has enabled him to devise a method of study of the highest value. That it has received the approbation of the illustrious HEAD of that school, and the benefit of three years practical experience under his immediate observation, must powerfully recommend it to the English student of chemistry. Whoever is desirous of obtaining the knowledge necessary to become a practical chemist, will be in no small degree indebted to Dr. Fresenius for the facilities thus afforded him. Every one who knows anything of Giessen, will bear testimony to the rigid economy of time, and the resolute adoption of every improvement in method which characterise that school, and serve to accomplish the many chemists annually flocking there for the completion of their studies. The author, in his preface to the first edition, tells us that he was led to compose this volume upon perceiving that the larger works on chemical analysis, such as H. Rose's, Duflos', and others, although admirable in themselves, present great difficulties to beginners, which difficulties may be summed up under three heads; 1st, Too great copiousness and detail; 2nd, The absence of explanations of the causes of phenomena, i. e. the *theory* of the operations and reactions; and 3rd, The omission altogether of many substances of very frequent occurrence, especially in the operations of the pharmaceutist, such as the organic acids, &c.

In avoiding these objections to former works on chemical analysis, Dr. Fresenius, I think, is not chargeable with having fallen into the opposite extreme of being too concise or elementary.

The student may, perhaps, at first be disappointed in taking up this work, to find that there are no tables constructed to furnish him at a glance with all he is desirous to know of tests and reactions, and to save him, as he may think, trouble and time. But this has not arisen from oversight; the question of the advantage or disadvantage of tables to the student has been fully considered, and the author has decided,—and the decision is borne out by the highest authorities,—that such tables serve no really good purpose; they rather, on the contrary, supply but very superficial information, and satisfy the student before they have really informed him. The information contained in this work, like every other professing to teach a practical science, requires application and perseverance to attain; but if begun at the beginning, if the student will carefully go over the necessary preliminary facts, the examination of his tests, and the reaction of the simple bodies consecutively, and make himself master of this very simple and elementary part of the course, he will find few or no difficulties when entering upon the more elaborate, and—what might appear, without this preparation—complex and intricate processes of the second part, the analysis of compound bodies. It is altogether another question whether the student should or should not exercise himself and his memory by tabulating the results of his experiments as he proceeds; and to this question we reply in the affirmative; but it must be left to individuals to act in this, according to their own judgment, and their own feeling of its necessity.

In the preface to the Second Edition, Dr. Fresenius tells us that his work has met with much success, having been adopted in the Pharmaceutical Institution of Bonn, &c., as well as in the laboratory of Giessen; and that he has improved it by many corrections and additions.

For my own part, I may be allowed to observe that the English edition was undertaken by the express desire of Professor Liebig, who kindly recommended its being intrusted to my care. The author has supplied me with many corrections, and some additions, and the hope is shared by us in common that it will facilitate the study of analytical chemistry to the English student, and in every way serve to promote the interests of the science.

J. LLOYD BULLOCK.

22, *Conduit Street*, *October* 1, 1843.

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ELEMENTARY INSTRUCTION

IN

QUALITATIVE CHEMICAL ANALYSIS.

PRELIMINARY REMARKS.

DEFINITION, PURPOSES, OBJECT, AND IMPORTANCE OF QUALITATIVE CHEMICAL ANALYSIS, AND CONDITIONS WHEREON A SUCCESSFUL STUDY OF THIS SCIENCE DEPENDS.

CHEMISTRY is that science which treats of the various substances constituting our earth, of their composition and decomposition, and of their mutual relations and deportment in general. A special branch of this science is designated by the name of *analytical chemistry*, inasmuch as it has a definite object in view, viz. the analysis of compound bodies, and the investigation of their constituents. If this investigation is confined to the *nature* and *properties* of the latter, the analysis is called *qualitative;* but if the *quantity* of every individual element is to be ascertained, the analysis is termed *quantitative.* The object of qualitative analysis, therefore, is to exhibit the constituent parts of an unknown substance in forms *already known*, and which consequently admit of safe inferences as to the nature of every individual element. The value of its method depends on two circumstances, viz. it must attain the object in view with unerring certainty, and in the most expeditious manner. Whereas, it is the object of quantitative analysis, to exhibit the elements, revealed by the qualitative investigation, in such forms as admit of the most accurate determination of their individual, and proportional, amount or weight.

The ways and means by which these distinct objects are respectively attained, differ much from each other. It is obvious, therefore, that the study of qualitative analysis must be separated from that of quantitative analysis, and, as a matter of course, must precede it.

Having thus generally defined the design and objects of qualitative analysis, I will now proceed to discuss briefly, in the first place, the preliminary information which qualifies students to cultivate this branch of science successfully, the rank which it occupies in chemistry, the objects to which it applies, and the advantages derived from it; and, in the second place, the main points whereon its study is based, and the principal parts into which it is distributed.

It is, above all, absolutely indispensable for the pursuit of qualitative investigations, that the student should possess some knowledge of the chemical *elements*, and of their most important combinations, as well as of the principles of chemistry in general, combined with a certain readiness in the apprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student combines with these qualifications the habit of invariably ascribing the failures with which he may happen to meet, to some error or defect in his operations, or, in other words, to the absence of some condition or other indispensable to the success of the experiment,—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit,—he possesses every requisite to render his study of analytical chemistry successful.

Now, although chemical analysis is thus based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we must consider it as a kind of *corner stone,* upon which the entire structure of this science rests; for it is almost of equal importance for all branches of theoretical, as well as of practical chemistry; and I need not expatiate here on the advantages which the physician, the apothecary, the mineralogist, the rational farmer, the manufacturer, the artisan, and many others, derive from analytical chemistry.

This alone would be sufficient reason to recommend a thorough and diligent study of this branch of science, even if its cultivation lacked those attractions which it unquestionably possesses for every one who devotes himself zealously and ardently to it: The human mind is constantly striving for the attainment of truth; it delights in the solution of enigmas, and where do we meet with a greater variety of problems, more or less difficult of solution, than in the province of chemistry? But as a problem, for which, after long pondering, we fail to discover the key, wearies and discourages the mind,—so, in like manner, do our chemical investigations, if we fail to attain the object in view, if our results do not bear the stamp of truth,—of unquestionable certainty. A *half-knowledge* is therefore, as indeed in every department of science, but more especially *here,* to be considered worse than no knowledge at all; and a mere *superficial* cultivation of chemical analysis is consequently to be particularly guarded against.

A qualitative investigation may be made with a twofold view, viz. either, 1st, to prove that a certain definite body is or is not contained in a substance, e. g. lead in wine; or, 2nd, to ascertain *all* the constituents of a chemical compound or mixture. Any substance whatever may, of course, become the object of a chemical analysis.

In the present work, however, we purpose to confine ourselves to those elements and compounds which are employed in pharmacy, in the arts and trades; viz.

I. Bases.

Potass, Soda, Ammonia, Barytes, Strontia, Lime, Magnesia, *Alumina, Oxide of Chromium, Oxide of Zinc, Protoxide of Manganese, Protoxide of Cobalt, Protoxide of Nickel, Protoxide of Iron, Peroxide of Iron, Oxide of Cadmium, Oxide of Lead, Oxide of Bismuth, Oxide of Copper, Oxide of Silver, Protoxide of Mercury, Peroxide of Mercury, Peroxide of Platinum, Peroxide of Gold, Protoxide of Tin, Peroxide of Tin, Oxide of Antimony.*

II. ACIDS.

Sulphuric Acid, Nitric Acid, Phosphoric Acid, Arsenious Acid, Arsenic Acid, Boracic Acid, Carbonic Acid, Chromic Acid, Chloric Acid, Silicic Acid, Oxalic Acid, Tartaric Acid, Paratartaric or Racemic Acid, Citric Acid, Malic Acid, Benzoic Acid, Succinic Acid, Acetic Acid, Formic Acid.

III. SALT-RADICALS AND NON-METALLIC ELEMENTS.

Chlorine, Iodine, Bromine, Cyanogen, Fluorine, Sulphur, Carbon.

The subject of qualitative analysis is most properly divided into four principal parts; viz.

1. THE ANALYTICAL OPERATIONS.
2. THE REAGENTS AND THE MODE OF THEIR APPLICATION.
3. THE DEPORTMENT OF VARIOUS BODIES WITH REAGENTS.
4. THE SYSTEMATIC COURSE AND METHOD OF QUALITATIVE ANALYSIS.

It will now be readily understood that the pursuit of chemical analysis requires practical skill and ability, as well as theoretical knowledge; and that, consequently, a mere speculative study of it can be as little expected to lead to success as purely empirical experiments. To render the desired end attainable, theory and practice must be combined.

CHAPTER I.

OPERATIONS.

§ 1.

The operations of analytical chemistry are essentially the same as those of synthetical chemistry, although modified, of course, to a certain extent, according with the object we have in view, and the quantities which we have to operate upon, in analytical investigations.

The following are the principal operations occurring in qualitative analysis.

§ 2.

1. SOLUTION.

The term "*solution*," in its widest sense, is applied to the perfect union of a fluid with any substance, no matter whether gaseous, liquid, or solid. But we call solution more properly *absorption* when the dissolved substance is *gaseous;* and when *liquid*, the term *mixture* is more frequently made use of. The application of the term solution, in its usual and more restricted sense, is confined to the perfect union of a *solid* substance with a fluid.

The more minutely we divide any substance to be dissolved, the more we facilitate its solution. The liquid, by means of which solution is effected, is called the *solvent*. We term the solution *chemical*, if the solvent enters into chemical combination with the substance dissolved, *simple*, if no definite combination takes place.

In a *simple* solution, the dissolved body exists in a free state, and possessed of all its original properties, except those dependent on its form and cohesion; it separates unaltered, when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt in this case imparts its peculiar taste to the water, and on evaporating the latter, we re-obtain common salt in its original form. A simple solution is called *saturated*, when the solvent has received as much as it can hold of the dissolved substance. But as fluids dissolve generally larger quantities of a substance, the higher their temperature, the term *saturated*, as applied to *simple* solutions, is only relative, and refers invariably to a certain temperature. It may be laid down as a general rule, that elevation of temperature facilitates and accelerates simple solution.

A *chemical* solution contains the substance dissolved, not in the same state, nor possessed of the same properties as before; the dissolved body is no longer free, but intimately combined with the solvent, the latter has also lost its original properties; a new substance has thus been produced, and the solution manifests therefore now the properties of this new substance. A chemical solution also may be *accelerated* by elevation of temperature, and this is indeed usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same, in proportion to a given quantity of the solvent, whatever may be the difference of temperature — the combining proportions of substances being invariable, and altogether independent of the gradations of temperature.

The reason of this is, that in chemical solution, the solvent and the body upon which it acts have invariably opposite properties, which they strive mutually to neutralize. Further solution ceases as soon as this tendency of mutual neutralization is satisfied. The solution is in this case said to be saturated, or more properly *neutralized,* and the point which denotes it to be so, is termed the point of saturation or neutralization. The substances which produce chemical solutions are, in most cases, either acids or alkalies. They all require, in the first place, to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present: e. g. when an aqueous solution of acetic acid is brought into contact with oxide of lead, there ensues, first, a chemical combination of the acid with the oxide, and finally a simple solution of the thereby produced acetate of lead in the water of the menstruum.

Crystallization and precipitation are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both depend on the same cause, viz. on the absence of a solvent, it is impossible to assign exact limits to either; in many cases they merge into one another. We must, however, consider them separately here, since they differ essentially in their extreme forms; and, moreover, since the special objects which we purpose to attain by their application are, in most cases, very distinct.

§ 3.

2. CRYSTALLIZATION.

We understand by the term crystallization, in a more general sense, every operation, or process, whereby bodies are induced to pass from the fluid to the solid state, and to assume certain regular, determinate, geometrical figures. But, as these figures, which we call *crystals*, are the more regular, and consequently the more perfect, the more slowly the operation is carried on, we always connect with the term " crystallization," the accessory idea of a *slow* separation,—of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangement of the ultimate constituent particles of bodies (*molecules* or *atoms*) ; it can only take place, therefore, if these atoms possess perfect freedom of motion, and thus, in general, only when a substance passes from the fluid or gaseous to the solid state. Those cases, in which crystallization is induced by the simple ignition, or softening of a solid body, are to be considered as exceptions,—thus, for instance, barley-sugar becomes white and opaque (crystallized) when moistened.

To induce crystallization, we have to remove the causes of the fluid or gaseous form of a substance. These causes are, either *heat alone*, e. g. in fused metals, or *solvents alone*, as in an aqueous solution of common salt ; or *both combined*, as in a hot and saturated aqueous solution of nitrate of potass. In the first case, we obtain crystals by cooling the fused mass ; in the second, by evaporating the menstruum ; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of the crystals, are called *mother waters*, or *mother liquors*. The term *amorphous* is applied to such solid bodies as have no crystalline form.

We induce crystallization generally, either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum.

§ 4.

3. PRECIPITATION.

This operation differs from crystallization inasmuch as in precipitation the dissolved substance is converted to the solid state, not in a slow and gradual manner, but *suddenly* ; it is a matter of perfect indifference, as regards the application of the term precipitation to the process, whether this substance is crystalline or amorphous, whether it gravitates to the bottom of the vessel, or ascends or remains suspended in the liquid. Precipitation is caused either by modification of the solvent—thus sulphate of lime (gypsum) separates immediately from its solution in water upon the addition of alcohol—or it ensues in consequence of the separation of an educt insoluble in the menstruum ; thus, when ammonia is added to a solution of sulphate of alumina, the latter salt is decomposed, and the alumina, not being soluble in water, precipitates. Precipitation takes place also when, by the action of simple or double chemical affinity, new combinations ensue which are insoluble in the menstruum; thus, oxalate of lime precipitates upon adding oxalic acid to a solution of acetate of lime,—chromate of lead upon mixing chromate of potash with nitrate of lead. In decompositions of this kind, induced by simple, or double affinity, one of the new compounds remains generally in solution, and the same is sometimes the case with the educt,—thus in the instances just mentioned, the sulphate of ammonia, the acetic acid, and the nitrate of potass, remain in solution. It may, however, happen also that both product and educt, or the two products, precipitate, and that nothing remains in solution ; this is the case, for instance, when a solution of sulphate of magnesia is mixed with water of barytes ; or a solution of sulphate of silver with chloride of barium.

Precipitation is applied for the same purposes as crystallization, viz. either to obtain a substance in the solid form, or to separate it from other substances dissolved in the same menstruum. But in qualitative analysis we resort to this operation more particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment, which they exhibit when precipitated, either in an isolated state, or combined with other substances. The solid body separated by this process, is called the *precipitate,* and the substance, which acts as the immediate cause of its separation, is termed the *precipitant*. For the sake of a more particular designation, we apply various terms to precipitates, according to their different nature; thus we distinguish crystalline, pulverulent, flocculent, curdy, gelatinous, precipitates, &c. &c.

The terms *turbid, turbidity,* are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. We may generally promote the separation of a precipitate by strongly agitating the menstruum, and also by elevating its temperature. The vessels used for the purpose of precipitation should therefore, if possible, admit of both these operations. In qualitative analysis we employ principally tubes of thin glass, closed at the bottom, such as are usually called test-tubes, or test-cylinders, (§ 14. 7.); these enable us, moreover, to operate upon very minute quantities, to inspect the whole process, and to observe the color of liquids and precipitates.

The two operations described at § 5 and 6, viz. *filtration* and *decantation,* serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. FILTRATION.

This operation consists simply in passing the fluid from which we wish to remove the mechanically-suspended solid particles through a filtering apparatus, formed usually by a properly-arranged piece of unsized paper, supported by a funnel; an apparatus of this description allows the fluid to trickle through with ease, whilst it retains the solid particles completely. We employ smooth filters and plaited filters: the former, in cases where the defiltrated solid substance is to be made use of; the latter, when we merely wish to clear the solution. Smooth filters are prepared by double folding of a circular piece of paper in such a manner, that the folds form right angles. The preparation of plaited filters is more properly a matter for ocular demonstration than for description. In very precise operations, the filters must not project over the brim of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but it renders the solid particles less liable to pass through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially from iron and lime. It is advisable always to keep two kinds, one of greater density for the separation of very finely-divided precipitates, and one of greater porosity for the speedy separation of grosser particles. The funnels must be either of glass or of porcelain. (§ 14. 10.)

§ 6.

5. DECANTATION.

This operation is frequently resorted to instead of filtration, when the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; since, in that case, they will speedily subside to the bottom, rendering it easy, either to decant the supernatant liquid by simply inclining the vessel, or to remove it by means of a syphon.

In cases where filtration or decantation are applied for the purpose of obtaining the solid substance, the latter must be freed, subsequently, by repeated *washing* from the liquid still adhering to it. This operation is also termed *edulcoration* or *rinsing*. The edulcoration of precipitates collected in a filter is usually effected by means of a syringe bottle, such as is represented by Figure 1.

FIG. 1.

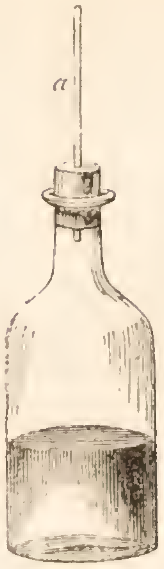
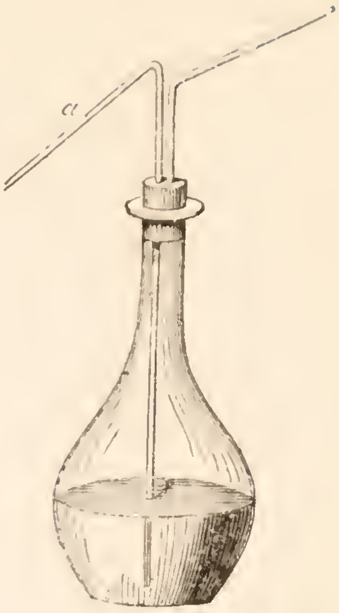


FIG. 2.



The syringe bottle illustrated by Fig. 1, consists of a flask, closed with a perforated cork, into which is adapted a small glass tube, drawn out to a fine point at the top (*a*). If air be blown into the flask through this tube, and, when the air is sufficiently compressed, the flask be reversed, so as to immerse the inner aperture of the tube in the water, a fine jet of water will be expelled with a certain degree of force; this contrivance is admirably adapted for rinsing precipitates.—Fig. 2. represents a syringe bottle of different construction; this is used to wash precipitates with boiling water; it affords, moreover, this advantage, that it enables the operator to produce a continuous stream of water. The engraving needs no explanation,—the tube *a* is drawn out *into a fine point* at its anterior aperture.

There are four operations which serve to separate volatile substances from less volatile, or from fixed bodies, viz. EVAPORATION, DISTILLATION, IGNITION, and SUBLIMATION. The two former of these operations are applied exclusively to fluids, the two latter exclusively to solids.

§ 7.

6. EVAPORATION.

This operation is of very frequent occurrence. It serves to separate volatile fluids from less volatile, or from fixed bodies, (no matter whether solid or fluid,) in cases where the residuary substance alone is of importance, whilst the evaporating matter is entirely disregarded ;—thus, for instance, we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to induce the salt to crystallize; we resort to this process also for the purpose of removing the whole of the water of the menstruum from the solution of a non-crystalline substance, so as to obtain the latter in a solid form, &c. &c. The evaporated water is entirely disregarded in either of these cases, and the only object in view is, to obtain, in the former case, a more concentrated fluid, and, in the latter, a dry substance. These objects are invariably attained by converting the fluid which is to be removed into the gaseous state ; and this generally by the application of heat; sometimes, also, by leaving the fluid for a certain time in contact with the atmosphere, or with confined air, which is constantly kept dry by hygroscopic substances ; or, finally, in many cases, by placing the fluid in rarified air, with simultaneous application of hygroscopic substances. The process of heating is conducted either over an open fire, (as coal-fire or flame of spirits of wine,) or in the sand-bath, or by means of steam, (in the water-bath,) &c. &c. Concentrated sulphuric acid, quick lime, and chloride of calcium, are the cheapest and most efficient hygroscopic substances. The vessels used in evaporation are made of porcelain, glass, platinum, or silver, and have usually the shape of a dish or shallow basin.

§ 8.

7. DISTILLATION.

This operation serves to separate a volatile liquid from a less volatile or fixed substance, (no matter whether solid or fluid,) and subsequently to recover the evaporated fluid. In order to attain this object, it is necessary to reconvert the liquid from the gaseous form in which it evaporates into the fluid state. A distilling apparatus consists, consequently, of three parts, no matter whether admitting of separation or not. These three parts are—1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor; 2nd, an apparatus in which this vapor is cooled again or *condensed*, and thus reconverted to the fluid state; and 3rd, a vessel which receives the thus reproduced fluid, (the distillate). In distillation on a small scale, we employ generally small glass retorts and receivers, but for the distillation of large quantities, we use either a metallic apparatus,—a copper still with helmet, and condensing-tube of tin, —or large glass retorts.

§ 9.

8. IGNITION.

Ignition is, in a certain measure, for solid bodies, what evaporation is with regard to fluids; since it serves (at least generally) to separate volatile substances from less volatile, or from fixed bodies, in cases where the residuary substance alone is of importance. Ignition always requires the application of a high temperature, and in this it differs from exsiccation. The form or state which the eliminated substance assumes on cooling, is a matter of perfect indifference as to the term we apply to the operation.

The elimination of a volatile substance is the most frequent purpose of ignition. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus the oxide of chromium is converted by ignition into its insoluble modification, &c. &c.—Crucibles are the vessels made use of in ignition. In analytical experiments we select, according to the substances to be ignited, either porcelain, platinum, or silver crucibles. In operations on a large scale, we use either hessian, or black-lead crucibles. The necessary heat is derived either from a charcoal-fire or, in experiments on a small scale, generally from a BERZELIUS' spirit-lamp.

§ 10.

9. SUBLIMATION.

The term *sublimation* designates that process which serves to expand solid bodies into vapor, by the application of heat, and subsequently to recondense the vapor to the solid state, by refrigeration ;—the substance thus volatilized and recondensed is called a *sublimate*. Sublimation is consequently a *distillation of solid bodies*. We have recourse to this process mostly to effect the separation of substances possessed of different degrees of volatility. Its application is of the highest importance in analysis for the detection of several substances, e. g. of arsenic. The vessels used in sublimation are of various shapes, according to the different degrees of volatility of the substances we have to operate upon. In sublimation for analytical purposes we employ generally glass tubes closed at both ends.

§ 11.

10. FUSION AND FLUXING.

We designate by the term " fusion," the conversion of a solid substance into a fluid form, by the application of heat; fusion is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term " fluxing " is applied to this process in cases where substances, either altogether insoluble, or very difficult of solution in water and acids, are, by fusion, in conjunction with some other body, modified or decomposed in such a manner, that they, or the new-formed compounds, subsequently admit of solution in water or acids. Fusion and fluxing are conducted either in porcelain, silver, or platinum crucibles, according to the nature of the analysed compound. Should a Berzelius' spirit-lamp fail to produce the necessary degree of heat, the crucible containing the mixture intended for fusion, is to be introduced into a larger, hessian crucible, and the latter exposed to a charcoal or coke fire.

The application of fluxing is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates. The flux most commonly used is carbonate of soda, or carbonate of potass, or, better still, a mixture of both, in equal atomic proportions, (vide § 76). In certain cases, hydrate of barytes is used instead of the alkaline carbonates, (vide § 77). But in either case the operation is conducted in platinum crucibles.

I have to add here, a few precautionary rules for the prevention of damage to the platinum vessels used in these operations. No substance, evolving chlorine, ought to be treated in platinum vessels; no nitrate of potass, caustic potass, metals, sulphurets, or alkaline cyanides, should be fused in such vessels, nor ought readily deoxidizable metallic oxides, organic metallic salts, or phosphates, to be ignited in them in the presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them directly to an intense charcoal fire, since the action of the ashes, under such circumstances, gives readily rise to the formation of silicide of platinum, which renders the vessels brittle.

I have still to mention, in this place, the following operation, which bears some affinity to fusion.

§ 12.

11. DEFLAGRATION.

We understand by the term "*deflagration*," in a more extended sense, every process of decomposition attended with noise or detonation,—(the *cause* of the decomposition is a matter of perfect indifference as regards the application of the term in this sense).

We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another admixed substance—(usually of a nitrate or chlorate,)—and connect with it the idea of sudden and violent combustion, attended with vivid ignition and noise or detonation. Deflagration is resorted to either to produce a certain oxide,—thus sulphuret of arsenic is deflagrated with nitrate of potass to obtain arseniate of potass;—or it is applied to prove the presence or absence of a certain substance,—thus salts are tested for nitric or chloric acid by fusing them in conjunction with cyanide of potassium, and observing whether this process will cause deflagration or not, &c. &c.

To attain the former object, the perfectly dry mixture of the substance under examination and of the deflagrating agent, is to be projected, in small portions, into a red-hot crucible. Experiments of the latter description are invariably made upon very minute quantities; the process is, in such cases, best conducted on a piece of thin platinum plate, or in a small spoon.

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§ 13.

12. The use of the blow-pipe.

This operation belongs exclusively to the province of analytical chemistry, and is of paramount importance in many analytical processes. We have to examine here, 1, the apparatus; 2, the mode of its application; and 3, the results of the operation.

The blow-pipe is a small instrument, usually made of brass. It was originally used by metallurgists for the purpose of soldering, whence it derived the name of "soldering pipe"—*Löthrohr*—by which the Germans designate it. It consists of three distinct parts; viz. 1st, a tube through which air is blown from the mouth; 2nd, a small vessel into which this tube is ground air-tight,—(this vessel serves to collect and retain the moisture of the air blown into the tube);—and 3rd, a smaller tube, which is likewise closely fitted into this vessel, and forms a right angle with the large tube; this small tube has a very fine aperture at its anterior extremity. (§ 14. 3.) The blow-pipe serves to conduct a fine and continuous stream of air into the flame of a candle or lamp. Such a flame presents, under ordinary circumstances, three distinct parts to the eye; viz, 1st, a dark nucleus in the centre; 2nd, a luminous part surrounding this nucleus; and 3rd, a kind of mantle encircling the whole flame, and but feebly luminous. The dark nucleus is formed by the gases which the heat evolves from the fuel; these gases cannot burn here, owing to want of oxygen. In the luminous sphere they come into contact with a certain amount of oxygen, although insufficient for their complete combustion. The hydrogen of the carburetted hydrogen gases evolved burns therefore principally here, whilst the carbon separates in a state of intense white heat, causing thus the luminousness of this part. In the outer coat, the access of air is no longer limited, and all the gases, not yet consumed, are consumed. This part of the flame is the hottest. Oxidizable bodies oxidize, therefore, with the greatest possible rapidity, when placed in it, since all the conditions of oxidation are here united, viz. high temperature, and an unlimited supply of oxygen. This part of the flame is accordingly called the *oxidizing flame.*

On the other hand, oxides having a tendency to yield up their oxygen, suffer *reduction,* when placed within the *luminous* part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed carburetted hydrogen present in this sphere. The luminous part of the flame is therefore called the *reducing flame.*

Now, if we conduct a fine stream of air into a flame, we have oxygen, not merely around the outer, but also in the inner part. Combustion takes place, therefore, in both parts. But this stream of air rushing with a certain force into the flame, carries forward the gases evolved, mixes intimately with them, and effects their combustion at a certain distance from the aperture of the blow-pipe. This point, which is marked by a bluish light, is the hottest part of the whole flame, since the intimate intermixture of the air with the gases favors here the most complete combustion. The luminous part of the flame being thus surrounded on both sides by very hot flames, acquires likewise an extraordinary increase of heat; this elevation of temperature forms the principal object which we intend to attain by the application of the blow-pipe. The hottest part of the flame lies now, of course, somewhat beyond the apex of the inner nucleus. In a reducing flame of this description many bodies will fuse readily, which a common flame would fail to effect. The heat of the oxidizing flame also is considerably increased by the blow-pipe being more strongly concentrated upon one point.

For *fuel* we use either an oil-lamp, a wax candle, or a lamp fed with a solution of oil of turpentine in spirits of wine. A common spirit-lamp does not always produce the necessary degree of heat.

The *current* is to be produced with the cheek-muscles alone, and not with the lungs. The way of effecting this may be readily acquired by practising for some time to breathe calmly, with puffed up cheeks, and whilst holding the blow-pipe between the lips; a little practice and patience will soon enable the student to produce a continuous, even, and steady current.

The *supports* on which the substances to be examined are exposed to the blow-pipe flame, are generally either wood, charcoal, or platinum wire or plate. In the choice of charcoal intended for blow-pipe experiments, we have to look more particularly to the coal being thoroughly charred, because, if not so, it will split and throw off the substances placed on it, (vide § 79). The substances to be examined are put into small conical cavities scooped with a pen-knife, or with a little tin tube. We generally employ charcoal as a support, when we want to reduce a metallic oxide, or to ascertain the degree of fusibility of a substance.

Metals which are volatile at the heat of the ordinary flame, evaporate wholly, or in part, upon the reduction of their oxides. But these metallic vapors are reoxidized in passing through the outer flame, and the oxide thus produced forms a slight incrustation around the substance upon the charcoal. Many of these incrustations exhibit characteristic colors which serve to assist in the detection of the metals.

The platinum wire, as well as the platinum plate, should be selected rather thin. (Vide § 14, 5 and 6.) We make use of platinum wire generally when fusing bodies in conjunction with fluxes, (vide § 82 and 83,) for the purpose of inferring their nature from the color and other properties of the button produced.

What renders the application of the blow-pipe particularly useful in chemical experiments, is the great facility with which the intended results are attained. The results are of a twofold kind, viz. either they afford us simply an insight into the general properties of the examined body, and enable us accordingly only to determine the *class* to which it belongs, i. e. whether it is fixed, volatile, fusible, &c. &c.; or the phenomena which we observe enable us at once to recognise the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the individual substances with reagents.

APPENDIX TO THE FIRST CHAPTER.

§ 14.

APPARATUS AND UTENSILS.

As the student cannot well be supposed to be acquainted with the apparatus, &c. &c. necessary for the processes of chemical analysis,—I deem it advisable to furnish him here with a list of those articles which are required for the performance of simple experiments and investigations. I shall at the same time point out the principal qualities which these articles should possess.

1. A Berzelius spirit-lamp. The vessel containing the spirit of wine should be connected with the wick-holder by means of a narrow tube, to avoid explosions;—the chimney should not be too narrow. The aperture through which the spirit of wine is poured should not be air-tight.

2. A lamp-stand with moveable rings and brackets.

3. A glass spirit-lamp with ground cover and brass wick-tube.

4. A brass blow-pipe with a mouth-piece made of horn or bone, (vide § 13.) The principal tube may be about seven inches in length, slightly varying, of course, according to the visual distance of the individual; the length of the smaller tube ought to be about two inches. Both must be ground air-tight into the small vessel which, as I have already stated at § 13, is intended to collect and retain the moisture of the air blown through the pipe. It is advisable to keep two small tubes at hand, one with a wider, and the

other with a narrower opening.—Most of the small tubes usually sold at the chemical instrument makers' are fitted simply with a small perforated platinum plate at their aperture. Those, however, which are provided with a finely perforated platinum cap are more durable; whenever the jet of these caps happens to be stopped up, the obstruction may be at once removed by igniting the cap before the blow-pipe.

5. A PLATINUM CRUCIBLE with ground cover; this should not be too deep, in proportion to its breadth.

6. A PLATINUM SPATULA, about two inches long and one inch in breadth; this should be of sufficient thickness, and as clean and smooth as possible.

7. A FEW PIECES OF PLATINUM WIRE, of the size of lute-strings, varying in length from three to four inches, and twisted at both ends into a small loop. It is advisable to keep these wires in a small phial filled with water, since most of the buttons produced by fusion or fluxing dissolve in water; by this means the wires may consequently be kept always clean.

8. A STAND WITH FROM TWELVE TO TWENTY TEST TUBES. The latter may vary from four to six or eight inches in length, and must be of different width. They should be made of thin white glass, and so well annealed, that they do not crack even though boiling water be poured into them. Their brim must be quite round, and slightly turned over; it ought to have no lip, since the latter is not of the slightest use, and prevents the tube from being closely stopped with the finger.

9. SEVERAL BEAKER GLASSES AND SMALL RETORTS of thin, well-annealed glass.

10. SEVERAL PORCELAIN EVAPORATING DISHES, AND A VARIETY OF SMALL PORCELAIN CRUCIBLES. Those of the royal manufacture of Berlin are unexceptionable, both in shape and durability.

11. SEVERAL GLASS FUNNELS of various sizes. They must be inclined at an angle of sixty degrees, and ought to merge into their tube at a definite angle.

12. A SYRINGE BOTTLE, capable of holding from twelve to sixteen ounces of water, (vide § 6.)

13. SEVERAL GLASS RODS AND TUBES. The latter may be bent, drawn out, &c., over a Berzelius spirit-lamp.

14. A selection of WATCH-GLASSES.

15. A small AGATE MORTAR.

16. Several small IRON SPOONS.

17. A pair of small PINCERS, with scissor-handles, the blades joining close together, and bent at their extremity at a right or slightly obtuse angle.

These should be varnished.

CHAPTER II.

REAGENTS.

§ 15.

VARIOUS phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color, in others precipitates are formed, sometimes effervescence takes place, and sometimes deflagration, &c. Now, if these phenomena are very striking, and attendant only upon the combination or decomposition of two definite bodies, it is obvious that the presence of the one of these bodies may be detected by means of the other: e. g. if we know that a white precipitate, of certain definite properties, is formed upon mixing barytes with sulphuric acid, it is clear that, if by adding barytes to any liquid we obtain a precipitate exhibiting these properties, we have to conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena, are called *reagents*.

These are divided into *general* and *special* reagents, according to the object attained by their application. By *general* reagents, we understand those which serve to determine the *class* or *group* to which the substance under examination belongs; and by *special* reagents those which serve to detect *individual* substances. That the limits between these two divisions cannot be drawn with any degree of precision, ought not to be considered a valid objection to this classification, which is simply intended to accustom the student to keep invariably in mind whether he purposes to ascertain the *group* to which the substance under examination belongs, or to determine the latter *individually*. The terms *characteristic* and *susceptible* are made use of to designate the two principal properties upon which the greater or less utility of a reagent depends. We call a reagent *characteristic*, if the alteration attendant upon the detection of the substance tested for is so distinctly marked as to admit of no mistake. Thus, iron is a characteristic reagent for copper, protochloride of tin for mercury, because the phenomena produced by these reagents, viz. the separation of metallic copper and of globules of mercury, admit of no mistake. We call a reagent *susceptible*, if its action is still clearly perceptible although but a very small quantity of the substance tested for be present, such is for instance the action of starch upon iodine. A great many reagents are *both* characteristic and susceptible; thus, for instance, perchloride of gold for protoxide of tin, ferrocyanide of potassium for copper, and peroxide of iron, &c. &c. I need scarcely mention that reagents must in general be chemically pure, i. e. they must contain no extraneous substance in admixture, since, if this be not the case, their indications cannot be relied upon. We must therefore make it an invariable rule to test the purity of reagents before we use them, no matter whether they be articles of our own production or of purchase. The instructions which I shall give in this respect when treating of the various reagents individually, refer, of course, only to such contaminations as are likely to arise from the mode of their respective preparation, but not to accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "*addition in excess*," "*supersaturation*," &c., often induce novices to suppose that they cannot add *too* much of the reagent, and thus many a one *fills* a test cylinder with acid simply to supersaturate a few drops of an alkaline fluid, whilst yet every drop of acid added, after the neutralization point has once been reached, is to be looked upon as an *excess* of acid. On the other hand, the addition of an insufficient amount is to be equally avoided, since a reagent, when added in insufficient quantity, often produces phenomena quite different from those which will appear if the same reagent be added in excess: e. g. a solution of perchloride of mercury yields a *white* precipitate, when tested with a *small* quantity of sulphuretted hydrogen; but when treated with sulphuretted hydrogen *in excess*, the precipitate is *black*. Experience has, however, proved that the most common mistake beginners are liable to is, to add the reagents too copiously. The reason why this over-addition must impair the accuracy of the results, is obvious; we need simply bear in mind, that the changes effected by reagents, are perceptible within certain limits only, and that accordingly they may be the more readily overlooked the more we approach these limits by diluting the fluid.

No special and definite rules can be given for avoiding this source of error; a general rule may, however, be laid down, and even this may be considered sufficient, to point out the proper measure in all, or at least in most cases. It is simply this: let the student always reflect, before the addition of a reagent, for what purpose he applies it, and what are the phenomena he intends to produce.

We divide reagents into two classes, according as the state of fluidity which is indispensable for the manifestation of the action of reagents upon the various bodies, is induced by the application of heat, or by means of liquid solvents; we have accordingly, 1, *Reagents in the humid way;* and 2, *Reagents in the dry way.*

For greater clearness and simplicity, we subdivide these two principal classes as follows :—

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. Reagents principally used as SIMPLE SOLVENTS.

b. Reagents principally used as CHEMICAL SOLVENTS.

c. Reagents which serve principally to separate, or otherwise to characterise groups of substances.

II. SPECIAL REAGENTS.

a. Reagents which serve principally for the detection of the BASES.

b. Reagents which serve principally for the detection of the ACIDS.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOW-PIPE REAGENTS.

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. Reagents principally used as simple solvents

§ 16.

1. WATER. (H O.)

Preparation.—Pure water is obtained by distilling spring-water from a copper-still, or from a glass retort. This distillation should not be carried beyond three-fourths of the quantity operated upon. Rain water received in the open air may in most cases be substituted for distilled water.

Tests.—Pure distilled water must leave no residue upon evaporation, nor should it alter the color of Georgina paper. (Vide § 24, 1. γ.) Nitrate of silver, chloride of barium, oxalate of ammonia, and lime-water, must not impair its transparency.

Uses.—We use water* principally as a simple solvent for a great variety of substances. It serves moreover to effect the transformation of several neutral metallic salts into soluble acid, and insoluble basic compounds; this is the case particularly with chloride of antimony and with the salts of bismuth.

§ 17.

2. ALCOHOL. ($C_4H_6O_2 = AeO + Aq.$)

Preparation.—Two sorts of alcohol are used in chemical analyses; viz. 1st, spirits of wine of 0·83 or 0·84 spec. gr. (*spiritus vini rectificatus* of the shops;) and 2nd, absolute alcohol. The latter may be prepared by distilling the former from fused chloride of calcium.

Tests.—Pure alcohol must completely volatilize, and ought not to cause the slightest smell of fousel oil, when rubbed between the hands; nor should it redden litmus paper.

Uses.—Many substances are soluble in alcohol, whilst others are insoluble in this menstruum. Alcohol is therefore frequently employed to effect the separation of the former from the latter, thus, for instance, to separate chloride of strontium from chloride of barium. Alcohol serves likewise to precipitate from aqueous solutions such substances as are insoluble in it, e. g. to precipitate malate of lime. We use alcohol, moreover, for the production of various kinds of ether, (especially of acetic ether, which is particularly characterized by its agreeable odor;) and likewise to co-operate with acids in the reduction of certain substances, for instance, of peroxide of lead, chromic acid, &c. &c. Alcohol serves also for the detection of various substances which impart a characteristic tint to its flame; such are especially boracic acid, strontia, soda, and potass.

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* In chemical experiments we use *exclusively* distilled water; whenever therefore the term "water" occurs in the present work, distilled water is meant.

§ 18.

3. ETHER. ($C_4 H_5 O = AeO.$)

Ether finds but very limited application in the analysis of inorganic bodies. It serves, in fact, almost exclusively to detect and isolate bromine, (§ 101, *b*,) and for this purpose the officinal ether of commerce is sufficiently pure and strong.

b. Reagents which are principally used as chemical solvents.

§ 19.

1. HYDROCHLORIC ACID. ($H Cl.$)

Preparation.—Pour a refrigerated mixture of 13½ parts of sulphuric acid with four parts of water, over eight parts of common salt in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath, until the evolution of gas ceases; conduct the evolved gas, by means of a double-limbed tube, into a flask containing twelve parts of water, and take care to keep this receiver constantly cool. To prevent the gas from receding, the tube ought to be permitted only to dip about one line into the water of the receiver. Should the sulphuric acid employed in the process contain nitric acid, the gas which passes over first, (and which in that case contains chlorine,) must be received separately. The hydrochloric acid produced is to be diluted with water until its specific gravity is from 1·11 to 1·12.

Tests.—Hydrochloric acid, intended for the purposes of chemical analysis, must be perfectly colorless, and leave no residue upon evaporation; it should not discolor indigo-solution upon ebullition. Chloride of barium ought not to produce any precipitate, neither in the highly diluted acid, (sulphuric acid,) nor even after ebullition with nitric acid, (sulphurous acid). Sulphuretted hydrogen must leave it unaltered. After neutralization with ammonia, and subsequent addition of a slight excess of acetic acid, ferrocyanide of potassium must not produce any precipitate in it, nor even impart to it the slightest tinge of blue.

Uses.—Hydrochloric acid serves as a solvent for a great many substances. It dissolves oxides and peroxides in the form of chlorides, the solution being, in the latter case, mostly attended with liberation of chlorine.—Salts, with insoluble or volatile acids, are also converted by hydrochloric acid into chlorides, with separation of the original acid; thus carbonate of lime is converted into chloride of calcium, with liberation of carbonic acid. Hydrochloric acid dissolves salts with non-volatile and soluble acids, *apparently* without decomposing them, (e. g. phosphate of lime); but we must suppose that solutions of this description arise from the formation of a soluble chloride and of a soluble acid salt of the acid of the dissolved compound; thus, for instance, in the case of phosphate of lime, we must assume that chloride of calcium and acid phosphate of lime are formed. This explanation, however, will not serve for salts with such acids as form no soluble acid compound with the base present; in such cases we must assume, either that the acid of the dissolved salt is present in the solution, in a free state, (borate of lime,) or that the hydrochloric acid acts *really* as a *simple* solvent. (Compare § 2.) Hydrochloric acid is also applied as a *special* reagent for the detection and separation of oxide of silver, protoxide of mercury, and lead, (vide infra,) and likewise for the detection of free ammonia (with which it produces dense white fumes of sal ammonia in the air.)

§ 20.

2. NITRIC ACID. (NO_5.)

Preparation.—The nitric acid of commerce contains almost invariably sulphuric acid and hydrochloric acid. To free it from these admixtures, solution of nitrate of silver is to be added to it, as long as any precipitate of chloride of silver continues to form; this precipitate is allowed to subside; the supernatant fluid is decanted into a retort, and distilled to within a small fraction of its whole amount. The distillate is then, if necessary, diluted with water until the specific gravity of the diluted acid is equal to 1·2.

Tests.—Pure nitric acid must be colorless, and, when evaporated on a platinum plate, leave no residue behind. The addition of solution of nitrate of barytes, or of nitrate of silver, must not cause the slightest turbidity in it. It is advisable to dilute the acid highly with water before adding these reagents, since otherwise nitrates will precipitate.

Uses.—Nitric acid serves, in the first place, as a chemical solvent for metals, oxides, sulphurets, oxygen salts, &c. The way in which the nitric acid effects the solution of metals and sulphurets, is this: it oxidizes these bodies first, at the expense of part of its own oxygen, and transforms the produced oxides subsequently into nitrates. Most oxides dissolve in nitric acid directly as nitrates, and the same is the case with most of the insoluble salts with weaker acids, the latter being expelled by the nitric acid in the process of solution. Salts with soluble non-volatile acids are dissolved by nitric acid in the same manner as by hydrochloric acid. (Vide § 19.) Nitric acid serves moreover very frequently as an oxidizing agent; thus it is used, for instance, to convert the protoxide of iron into the peroxide, to decompose hydriodic acid and the iodides, &c.

§ 21.

CHLORO-NITRIC ACID. AQUA REGIA. ($N\,Cl_2\,O_3$.)

Preparation.—One measure of pure nitric acid is mixed with from three to four measures of pure hydrochloric acid.

Uses.—When nitric acid is brought into contact with hydrochloric acid, a mutual decomposition of the two acids ensues, the transposition of their elements giving rise to the formation of water and of a new compound, to which Baudrimont, its discoverer, has assigned the name of *chloronitric acid;* this new compound is gaseous at the common temperature, and soluble in water; its composition is expressed by the formula $N\,Cl_2\,O_3$.

$$(2\,Cl\,H + N\,O_5 = N\,Cl_2\,O_3 + 2\,H\,O.)$$

This decomposition ceases when the fluid is saturated with the chloronitric acid gas, but it recommences the instant that this state of saturation is disturbed by the application of heat, or in consequence of the decomposition of the chloronitric acid. The chlorine and part of the oxygen of this acid are held in combination by a very feeble affinity only; the presence of this acid renders aqua regia therefore the most powerful solvent for metals, with the exception of those which form insoluble compounds with chlorine.—Aqua regia serves principally to effect the solution of gold and platinum, (which metals are insoluble both in hydrochloric and nitric acid,) and the decomposition of divers sulphurets, e. g. cinnabar, &c. &c.

§ 22.

4. ACETIC ACID. ($C_4 H_3 O_3 = \overline{A}$.)

Preparation.—Triturate ten parts of crystallized neutral acetate of lead, with three parts of effloresced sulphate of soda; introduce the powder into a retort, add a refrigerated mixture of two and a half parts of sulphuric acid with an equal weight of water, and distil to dryness in a sand-bath. The most appropriate way of connecting the receiver with the retort, is by means of a LIEBIG'S condensing apparatus.

Tests.—Pure acetic acid must leave no residue upon evaporation. The diluted acid ought not to be precipitated by sulphuretted hydrogen, nor by solution of nitrate of silver or nitrate of barytes, by the latter not even after previous ebullition with nitric acid. Should nitrate of barytes produce a precipitate in acetic acid which has been previously boiled with nitric acid, this is a proof of the presence of sulphurous acid; the acetic acid in such cases is to be digested with brown peroxide of lead, and subsequently redistilled. Pure acetic acid, moreover, must not decolor solution of indigo. (Vide § 102, *a.*)

Uses.—Acetic acid possesses a greater solvent power for some substances than for others;—it is used, accordingly, to separate the former from the latter; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. We apply acetic acid also for the acidulation of fluids, in cases where we wish to avoid the use of mineral acids.

§ 23.

5. CHLORIDE OF AMMONIUM. ($N\,H_4$, Cl.)

Hydrochlorate of Ammonia.—Muriate of Ammonia.—Sal Ammoniac.

Preparation.—The sal ammoniac of commerce may generally be purified by simple recrystallization. Should it contain iron, this may be removed by the following process: a small portion of sulphuret of ammonium is added to the solution of the sal ammoniac, and the precipitate which forms is allowed to subside; the fluid is then filtered off, and hydrochloric acid added to the filtrate, until the latter acquires a feebly acid reaction; the mixture is then heated to ebullition, filtered, saturated with ammonia, and finally crystallized. For use, one part of the salt is dissolved in eight parts of water.

Tests.—Solution of sal ammoniac, when evaporated on a platinum plate, should leave a residue, which must subsequently, upon continued application of heat, completely volatilize. It ought not to be affected by the action of sulphuret of ammonium. Its reaction should be perfectly neutral.

Uses.—Sal ammoniac serves principally to retain certain oxides, (e. g. protoxide of manganese, magnesia,) or salts, (e. g. tartrate of lime,) in solution, upon the precipitation of other oxides or salts by ammonia or some other reagent. This application of sal ammoniac is based upon the tendency of the ammoniacal salts to form double compounds with other salts. Sal ammoniac serves also to distinguish between precipitates possessed of similar properties, and thus, for instance, to distinguish the *basic phosphate of magnesia and ammonia* which is insoluble in sal ammoniac, from other precipitates of magnesia. We use sal ammoniac, moreover, to precipitate, from potass solutions, various substances which are soluble in potass, and insoluble in ammonia, for instance, alumina, oxide of chromium, &c. &c. In this process, the elements of the sal ammoniac transpose with those of the potass, and this transposition results in the formation of chloride of potassium, water, and ammonia. Sal ammoniac is applied also as a *special* reagent for the precipitation of platinum as ammonio-chloride of platinum.

c. Reagents which serve principally to separate or otherwise to characterize groups of substances.

§ 24.

1. REAGENT PAPERS.

a. BLUE LITMUS PAPER.

Preparation.—One part of litmus of commerce is to be digested with six parts of water; the solution is subsequently to be filtered, and the intensely blue filtrate divided into two equal parts; —the free alkali in the one part is then to be saturated by stirring with a glass rod which has been dipped previously into very dilute sulphuric acid, and repeating this process until the fluid begins to look red; the other part of the filtrate is now added to the reddened fluid, and the whole mixture poured out into a basin, where slips of fine unsized paper are finally drawn through it. These slips are afterwards suspended over threads, and left to dry. The color of litmus paper must be perfectly uniform, and neither too light nor too dark.

Uses.—Litmus paper serves to detect the presence of free acid in fluids, since acids change its blue colour to red. It is to be borne in mind, however, that the neutral salts of most of the heavy metallic oxides produce the same effect.

β. REDDENED LITMUS PAPER.

Preparation.—Blue tincture of litmus is stirred with a glass rod dipped previously into dilute sulphuric acid, and this process repeated until the fluid begins to look distinctly red. Slips of paper are then drawn through the tincture, and finally dried as at *a*. The dried slips must look distinctly red.

Uses.—Pure alkalies and alkaline earths, and likewise the sulphurets of these substances, restore the blue color of reddened litmus paper; alkaline carbonates and the soluble salts of several other weak acids, especially of boracic acid, possess the same property. This reagent serves therefore for the detection of these substances in general.

γ. GEORGINA PAPER.

Preparation. — The violet-colored petals of *Georgina purpurea* (purple dahlia) are boiled in water or digested with spirit of wine; the fluid is finally filtered, and slips of paper are drawn through the filtrate; the latter should be neither more nor less concentrated than is necessary to make the paper, after drying, appear of fine and rather light violet-blue color. Should the color too much incline to red, this may be remedied by adding a small amount of ammonia to the tincture.

Uses.—Georgina paper is reddened by acids, whilst alkalies impart a beautiful green tint to it. It is therefore an extremely convenient substitute both for the blue and the reddened litmus paper. This reagent, if properly prepared, is extremely susceptible for acids as well as for alkalies. Concentrated solutions of caustic alkalies turn Georgina paper yellow, by destroying the coloring matter.

δ. TURMERIC PAPER.

Preparation.—One part of bruised turmeric-root is digested and heated with six parts of dilute spirit of wine; the tincture obtained by this process is filtered, and slips of fine paper are dipped into it. The dried slips must exhibit a fine yellow tint.

Uses.—Turmeric paper serves, like reddened litmus paper and

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* Mr. A. S. Taylor has suggested that a very susceptible paper for detecting alkalies may be prepared by steeping it in an [illegible] infusion of rose petals.

Georgina paper, for the detection of free alkalies, &c. ; since they change its yellow color to brown. It is not quite so susceptible as the other reagent papers, but the change of color which it produces is highly characteristic, and is particularly perceptible in many *colored* liquids; we, therefore, cannot well dispense with turmeric paper. When testing with turmeric paper, it is to be borne in mind that, besides the substances enumerated at *β.*, several other bodies (boracic acid, for instance,) possess likewise the property of turning its yellow color to brown. All reagent papers are to be cut into slips, and kept in small, well-closed boxes, or stoppered phials.

§ 25.

2. SULPHURIC ACID. (SO_3.)

Sulphuric acid of commerce, freed from nitric acid by ebullition, is sufficiently pure for the purposes of qualitative analysis.* Should it, however, contain arsenic, this must be removed first before the acid can be applied for the detection of arsenic by Marsh's method. The following process will serve to effect this depuration. The acid is to be diluted with six times its amount of water, and the fluid saturated with sulphuretted hydrogen ; the mixture is then allowed to stand in a moderately warm place until it is perfectly clear, when the fluid is to be filtered off from the precipitated sulphuret of arsenic. The filtrate is finally boiled until it is perfectly inodorous.

Test.—Sulphuric acid, when boiled with a small portion of indigo solution, must not destroy the blue colour of the latter. When mixed with pure zinc and water, it must yield hydrogen which, on being passed through a red-hot tube, does not deposit the slightest trace of arsenic. (Compare § 95, *d.*)

Uses.—Sulphuric acid has to most bases a greater affinity than almost any other acid; it is therefore used principally for the liberation and expulsion of other acids, especially of phosphoric, boracic, hydrochloric, nitric, and acetic acid. It serves also for the liberation of iòdine from the iodides. In this process, it oxidizes the metals at the expense of its own oxygen, and is accordingly reduced to the state of sulphurous acid. Several substances which cannot exist in an anhydrous state (e. g. oxalic acid) are decomposed when brought into contact with concentrated sulphuric acid; this decomposition is owing to the great affinity which sulphuric acid possesses for water. The nature of the decomposed body may in such cases be determined by the liberated products of its decomposition. Sulphuric acid is, moreover, frequently used for the evolution of divers gases, more particularly of hydrogen and sulphuretted hydrogen. Sulphuric acid serves also as a *special* reagent for the detection of barytes, strontia, and lead; the acid intended for this purpose is to be diluted with four parts of water.

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* The sulphuric acid of commerce often contains lead, which renders it turbid when diluted; this may be removed by allowing the lead to subside, or by distillation.—Ed.

§ 26.

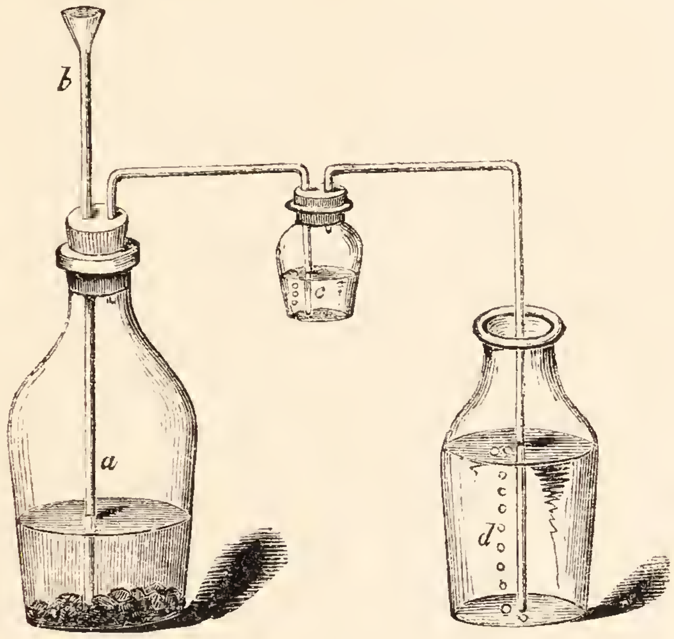
3. SULPHURETTED HYDROGEN. (H S.)

Preparation.—An intimate mixture of thirty parts of iron filings with twenty-one parts of flower of sulphur is gradually projected in small portions into a red-hot crucible, with this precaution, that the operator awaits always the incandescence of the last introduced portion, before proceeding to the addition of a fresh one. When the whole mixture has thus been introduced into the crucible, the latter is carefully covered, and allowed to continue a short time longer exposed to the fire.

Should the operator happen to possess a blast furnace or a well draughted wind furnace, he may procure a purer and superior kind of sulphuret of iron, by heating iron borings to the most intense redness in a hessian crucible, and projecting small lumps of sulphur upon the ignited mass, until the whole is converted into sulphuret of iron. A perforation in the bottom of the crucible will be found of some use in this process, since this will allow the sulphuret of iron to run off immediately upon its formation, when it may very conveniently be received in a coal shovel placed in the ash-pit.

The sulphuret of iron produced by either method is broken into lumps, and the latter are introduced into an evolution flask. (Vide Plate III. *a.*)

PLATE III.



Water is then poured into the flask, and concentrated sulphuric acid added through the funnel-tube *b*. The evolved gas is purified by transmitting it through some water contained in a small flask (*c*).

Sulphuretted hydrogen water (*solution of sulphuretted hydrogen*) is prepared by conducting the purified gas into a flask (*d*), filled to about three-fourths with water of the lowest possible temperature, and which has been previously freed from air by ebullition. This operation is continued until the water is completely saturated with sulphuretted hydrogen gas, which may be readily ascertained by closing the mouth of the flask with the thumb, and strongly agitating its contents: if, upon this, a pressure is felt from within tending to push the thumb off the aperture of the flask, the operation may be considered at an end; but if, on the contrary, the thumb feels sucked into the mouth of the flask, this is a sure sign that the water is still capable of absorbing more gas.

Sulphuretted hydrogen water must be kept in well closed vessels, since otherwise it will soon suffer complete decomposition. The best way of preserving it unaltered for a very long time is to pour the fresh prepared solution immediately into small phials, and to place the latter, carefully corked, in an inverted position, into small vessels filled with water.

Tests.—Pure sulphuretted hydrogen water ought to be perfectly clear, and should possess the odor of the gas in an eminent degree; when treated with perchloride of iron, it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it.

Uses.—Sulphuretted hydrogen has a strong tendency to transpose with metallic oxides into water and metallic sulphurets; which latter being mostly insoluble in water, are usually precipitated in this process of transposition. The conditions under which the precipitation of divers sulphurets ensues differ materially;—by altering or modifying these conditions, we may accordingly divide the whole of the precipitable metals into groups, as will be found explained at § 27. Sulphuretted hydrogen is therefore a most invaluable agent to effect the separation of metals into principal groups. Some of the precipitated sulphurets exhibit a characteristic color indicative of the individual metals which they respectively contain. Sulphuretted hydrogen serves thus more particularly for the special detection of tin, antimony, arsenic, cadmium, manganese, and zinc. For more ample information upon this point, I refer to the third section. The great facility with which sulphuretted hydrogen is decomposed, renders this substance likewise a useful reducing agent for many compounds; thus it serves, for instance, to reduce persalt of iron to the state of protosalt, chromic acid to the state of oxide, &c., &c. In such processes of reduction, the sulphur separates in the form of a fine white powder.

§ 27.

4. HYDROSULPHURET OF AMMONIA. ($N H_4 S, H S.$)

(*Double sulphuret of ammonium and hydrogen.*)

Preparation.—Transmit sulphuretted hydrogen gas through solution of ammonia, to complete saturation, consequently until the mixture ceases to precipitate a solution of sulphate of magnesia.

The hydrosulphuret of ammonia, thus prepared, must be kept in well-stoppered phials, since contact with the atmosphere would cause its decomposition.

Tests.—Hydrosulphuret of ammonia is colorless at first, and deposits no sulphur on being mixed with acids; when exposed to the contact of the air, it acquires a yellow tint, owing to the formation of pentasulphuret of ammonium. ($N H_4, S_5$.) This yellow coloration does not by any means render the reagent unfit for use; but it is to be borne in mind that it will now deposit sulphur when mixed with acids. Hydrosulphuret of ammonium must be transparent; upon the application of heat, it must volatilize without leaving the slightest residue; and, as already stated, it ought not to precipitate solution of sulphate of magnesia.

Uses.—I mentioned already in the preceding paragraph that the separation of the metallic oxides precipitable by sulphuretted hydrogen, and their consequent arrangement into groups, depends upon certain conditions respectively requisite for their precipitation. The *presence* of an alkali forms one of these conditions—its *absence* forms another—which means that certain sulphurets precipitate only when the menstruum is alkaline, because they are soluble in acids; whilst others precipitate only when the menstruum is acid, since they are soluble in alkaline sulphurets. Now the double sulphuret of ammonium and hydrogen—(which we will, in future, invariably call hydrosulphuret of ammonia)—may be looked upon as a reagent in which sulphuretted hydrogen acts in conjunction with ammonia; we have here accordingly the conditions requisite to effect the precipitation of the just now mentioned first group of sulphurets, combined with those requisites, either to *prevent* the precipitation of the sulphurets of the other group, or to effect their re-solution, when precipitated from acid solutions, by digesting the precipitate with the reagent. Hydrosulphuret of ammonia intended for the latter purpose must, in certain cases, contain an excess of sulphur.

Besides the sulphurets, the precipitation of which is effected by the joint action of sulphuretted hydrogen and of ammonia, hydrosulphuret of ammonia precipitates, by the sole action of its ammonia, alumina and oxide of chromium as hydrated oxides, and likewise substances contained in a state of simple solution in a free acid; thus it precipitates, for instance, phosphate of lime from its solution in hydrochloric acid;—this property of hydrosulphuret of ammonia must not be lost sight of in experiments.

§ 28.

5. SULPHURET OF POTASSIUM. ($KO, S_2O_2+2KS_2$.)

Preparation.—This reagent must be prepared fresh every time when needed for use. The best way of invariably ensuring the production of a sulphuret of potassium of uniform composition, is to divide a certain quantity of potass ley into two equal portions, to boil the one portion with sulphur in excess, to decant the dark yellow fluid from the undissolved sulphur, and to mix the decanted liquid with the other portion of the potass ley.

Uses.—Sulphuret of potassium is substituted for hydrosulphuret of ammonia, to effect the separation of sulphuret of copper from such compounds of sulphur as are soluble in alkaline sulphurets, from protosulphuret of tin, for instance, since sulphuret of copper is not quite insoluble in hydrosulphuret of ammonia.

§ 29.

6. POTASS. (KO.)

Preparation.—Dissolve one ounce of pure carbonate of potass (vide § 30) in twelve ounces of water, pour the solution into a clean iron pan, and heat to boiling. Keep the fluid in constant ebullition, and add hydrated lime in small portions until a sample of the mixture ceases to cause the slightest effervescence when filtered into hydrochloric acid. (Two parts of carbonate of potass require the hydrate of about one part of caustic lime.) When this point is attained, remove the pan from the fire, when the carbonate of lime formed in the process will quickly subside. Pass the supernatant fluid now through a filter of bleached linen, and evaporate the filtrate over a rapid fire in an iron pan or, better still, in a silver basin, until reduced to four ounces, which will accordingly give a specific gravity of 1.33.

Potass ley is most safely kept in a small flask, closed by means of ground glass caps instead of stoppers; in default of capped flasks, common phials with ground stoppers may be used, with this precaution, that a small slip of writing paper be rolled round the stopper, otherwise it will, after the lapse of a short time, be found impossible to take the stopper off.

Tests.—Pure potass ley must be colorless. After supersaturation with nitric acid, (which process should be attended with slight effervescence only,) it must yield no precipitate, neither with solution of chloride of barium nor with solution of nitrate of silver; nor ought the residue which remains upon evaporation to dryness leave any silicic acid when redissolved in water. Finally, potass ley ought not to be rendered turbid when heated with an equal measure of solution of sal ammoniac.

Uses.—The great affinity which potass possesses for acids renders this substance a powerful agent to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases which are insoluble in water. Many of the thus precipitated oxides redissolve in an excess of potass; such are, for instance, alumina, oxide of chromium, oxide of lead; whilst others remain undissolved, e. g. peroxide of iron, oxide of bismuth, &c., &c. Potass serves accordingly also as a means to separate the former from the latter. Potass possesses, moreover, a solvent power for many salts, (e. g. chromate of lead,) sulphurets, &c., &c., and enables us thus to separate and distinguish them from other substances. Many of the oxides precipitated by the action of potass exhibit a peculiar color or possess other characteristic properties which may serve to lead to the detection of the individual metal which they respectively contain; such are, for instance, the precipitates of protoxide of manganese, protoxide of iron, protoxide of mercury, &c., &c. Potass expels ammonia from its salts, and enables us thus to detect the latter substance by its odor, its reaction on vegetable colors, &c. &c.

§ 30.

7. CARBONATE OF POTASS. (KO, CO_2.)

Preparation.—Ignite purified and thoroughly-washed bitartrate of potass in an iron pan, to complete carbonization, boil the residue with water, filter the solution, and evaporate it to dryness in a clean iron pan, taking care towards the conclusion of the process to keep on stirring the mass without interruption; keep the dry salt in a well-closed phial. When required for use, dissolve one part of the dry salt in five parts of water.

Tests.—Carbonate of potass intended for analytical purposes must be perfectly white. Neither chloride of barium nor nitrate of silver must render its solution turbid, after supersaturation with nitric acid; nor ought the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, leave any silica when redissolved in water.

Uses.—With the exception of the alkalies, carbonate of potass precipitates the whole of the bases, most of them as carbonates, but some also as oxides. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of potass exhibit a characteristic color which may lead to the detection of the individual metals which they respectively contain. Solution of carbonate of potass serves moreover for the decomposition of many insoluble salts of the alkaline earths, or with metallic bases, and more particularly of those with organic acids; upon boiling such salts with carbonate of potass, there ensues double decomposition, the base of the analysed salt combining with the carbonic acid, whilst the liberated acid combines with the potass, and is thus obtained in solution in the form of a potass salt. Carbonate of potass is used also to saturate free acids, and thus to obtain them in the form of potass salts. This substance finally is used as *a special* reagent, in which capacity it serves to precipitate platinum from solutions containing hydrochloric acid.

§ 31.

8. AMMONIA. (NH_3.)

Preparation.—The apparatus illustrated by Plate III. (vide § 26) may likewise serve for the preparation of liquor of ammonia, with this modification, however, that no funnel tube being required in this process, the cork upon the flask *a* has only one perforation for the reception of the tube which serves to conduct the evolved ammonia into the washing bottle. The washing should contain only a very small amount of water, whilst the flask *d*, which is intended for the final reception of the washed gas, must contain ten parts of water. The operation commences by slaking four parts of caustic lime with $1\frac{1}{3}$ parts of water; the thus produced hydrate is introduced into *a*, and mixed with five parts of sal ammoniac in powder; water is then cautiously added sufficient to form the powder into lumps when agitated. The flask *a* is then connected with the rest of the apparatus, and placed in a sand-bath, the flask *d* standing in a vessel with cold water. The evolution of gas will now speedily ensue, upon the application of heat, which latter is to be continued until no more bubbles appear. The cork is quickly removed from the flask *a*, to prevent the receding of the fluid. The liquor of ammonia contained in the washing bottle is impure, but that contained in the receiver *d* is perfectly pure; it contains about 16 per cent. of ammonia, and has accordingly a specific gravity of about 0.93. It is to be kept in phials closed with ground stoppers.

Tests.—Liquor of ammonia must be colorless, and ought not to leave the slightest residue when evaporated on a watch-glass, nor should it cause the slightest turbidity in lime-water (carbonic acid). Neither solution of nitrate of barytes, nor solution of nitrate of silver, should render it turbid after supersaturation with nitric acid, nor should sulphuretted hydrogen impart to it the slightest color.

Uses.—Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in excess of ammonia as ammoniacal double salts, for instance, the oxides of zinc, cadmium, silver, copper, &c., &c., whilst others are insoluble in free ammonia. This reagent may serve, therefore, to separate and distinguish the former from the latter. Some of these precipitates, as well as their ammoniacal solutions, exhibit a peculiar color, which may at once lead to the detection of the individual metals which they respectively contain.

Many of those oxides which are precipitated by ammonia from neutral solutions, are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the formation of an ammoniacal salt. Compare § 23, chloride of ammonium.

§ 32.

9. CARBONATE OF AMMONIA. (NH_4O, CO_2.)

Preparation.—We use, for the purposes of chemical analysis, purified sesquicarbonate of ammonia, entirely free from any smell of animal oil, (such as is prepared on a large scale, by the sublimation of sal ammoniac and chalk). The outer and inner surface of the mass are to be carefully scraped. One part of this salt is to be dissolved in a mixture of four parts of water with one part of caustic liquor of ammonia.

Tests.—Pure carbonate of ammonia must completely volatilize. Neither solution of nitrate of barytes, nor solution of nitrate of silver, nor sulphuretted hydrogen, should color or precipitate it, after supersaturation with nitric acid.

Uses.—Carbonate of ammonia precipitates, like carbonate of potass, most metallic oxides and earths. The complete precipitation of many of them ensues equally only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner, carbonate of ammonia dissolves many hydrated oxides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent. This power of solution rests upon the tendency of the ammoniacal salts to form soluble double salts, which are indecomposable by free ammonia as well as by carbonate of ammonia.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions, many oxides which it precipitates from neutral solutions. (Compare § 31.) We use carbonate of ammonia, in chemical analysis, principally to effect the precipitation of barytes, strontia, and lime, and the separation of these substances from magnesia, since the latter substance is not precipitated by this reagent in the presence of ammoniacal salts.

§ 33.

10. CHLORIDE OF BARIUM. (Ba Cl.)

Preparation.—Six parts of finely levigated sulphate of barytes are mixed with one part of powdered charcoal and one and a half part of flour; the mixture is introduced into a hessian crucible, and the latter exposed to the strongest possible red heat. The fused and refrigerated mass is levigated; about nine-tenths of the powder is then boiled with four times its weight of water, and hydrochloric acid is added, until all effervescence of sulphuretted hydrogen ceases, and the fluid begins to manifest a feebly acid reaction. The last tenth of the powder is then added, and the boiling still continued for some time. The alkaline fluid is subsequently filtered, and the filtrate crystallized. The crystals when dry are digested and thoroughly washed with alcohol, redissolved in water, and the solution finally re-crystallized. For use, one part of the crystals is dissolved in ten parts of water.

Tests.—Pure chloride of barium must not alter vegetable colors, nor ought its solution to be colored or precipitated by sulphuretted hydrogen, nor by hydrosulphuret of ammonia. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered off from the precipitate formed upon the addition of the test fails to leave the slightest residue when evaporated on a platinum plate.

Uses.—Barytes forms with many acids soluble, with others, insoluble compounds. This property of barytes affords us a means of distinguishing the former acids, which are not precipitated by chloride of barium from the latter in the solution of the salts of which this reagent produces a precipitate. The deportment which the precipitated salts of barytes respectively manifest with other substances (acids) differs. Accordingly, by subjecting the salts to the action of such substances, we are enabled to subdivide the group of precipitable acids, and even to detect certain individual acids, and more particularly sulphuric acid. This renders chloride of barium one of our most important reagents.

§ 34.

11. NITRATE OF BARYTES. ($Ba\,O, N\,O_5$.)

Preparation.—A dilute solution of chloride of barium is boiled, and carbonate of ammonia added, as long as a precipitate continues to form, and accordingly until the liquid manifests an alkaline reaction. The carbonate of barytes obtained by this process is carefully washed, and subsequently projected into hot dilute nitric acid, until the fluid ceases to manifest an acid reaction. The solution is then filtered, and the filtrate subsequently evaporated to crystallization. For use, one part of the crystallized salt is dissolved in ten parts of water.

Tests.—The purity of nitrate of barytes is tested by the same means as that of chloride of barium (§ 33). Nitrate of silver must not render its solution turbid.

Uses.—Nitrate of barytes is analogous in its action to chloride of barium, and may be substituted for this latter substance in cases where it is desirable to avoid the presence of a metallic chloride.

§ 35.

CHLORIDE OF CALCIUM. ($Ca\,Cl.$)

Preparation.—Chalk is added to hot dilute hydrochloric acid, until all acid reaction ceases; the solution is then filtered, and some ammonia added to it; the mixture is allowed to stand a few hours, at a moderate heat, and is afterwards filtered; the filtrate is subsequently heated to boiling, and carbonate of ammonia added until the lime is completely precipitated; the precipitated carbonate of lime is to be thoroughly washed. A mixture of one part of pure hydrochloric acid with five parts of water is now heated and the washed carbonate of lime added to complete neutralization; the solution is boiled up several times, and subsequently filtered, and kept for use.

Tests.—Solution of chloride of calcium must be perfectly neutral, and neither be colored nor precipitated by hydrosulphuret of ammonia; nor ought it to evolve ammonia when mixed with potash or with hydrate of lime.

Uses.—Chloride of calcium is, in its action and application, analogous to chloride of barium. For, as the latter reagent is used to divide the *inorganic* acids into groups, so chloride of calcium serves in the same manner to effect the separation of the *organic* acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others. And, as is the case with the barytes precipitates, the different conditions under which the various insoluble lime salts are precipitated, enable us to subdivide the group of precipitable acids, and even to detect certain individual acids.

§ 36.

13. NITRATE OF SILVER. ($Ag\,O, N\,O_5$.)

Preparation.—To obtain nitrate of silver in a state of purity, silver alloyed with copper, a piece of standard coin, for instance, is dissolved in nitric acid. The solution is evaporated to dryness, and the residue fused in a small porcelain basin over a spirit-lamp, at a moderate heat, until the nitrate of copper is completely decomposed, that is, until the salt has completely lost its green color, even in the portions adhering to the upper sides of the basin, and the aqueous solution of a sample of it fails to turn blue upon addition of ammonia in excess. The mass is then allowed to cool, and subsequently boiled with water; the solution of nitrate of silver is filtered off from the insoluble oxide of copper, and the filtrate finally made to crystallize. One part of the crystals is dissolved in twenty parts of water, for use. The oxide of copper which remains upon the solution of the fused mass, contains invariably a slight admixture of silver. To recover this, the residuary oxide of copper is redissolved in nitric acid, and the silver subsequently precipitated from the solution in the form of chloride of silver.

Tests.—Solution of nitrate of silver must be completely precipitated by dilute hydrochloric acid, so that the fluid filtered off from the precipitated chloride of silver, leaves no residue when evaporated on a watch-glass, and is, moreover, neither precipitated nor colored by sulphuretted hydrogen.

Uses.—Oxide of silver forms with many acids soluble, with others insoluble compounds. Nitrate of silver may, therefore, serve, like chloride of barium, to effect the separation and arrangement of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute sulphuric acid; chloride, bromide, iodide and cyanide of silver are insoluble in that menstruum. Nitrate of silver is therefore a most excellent agent to distinguish and separate from all other acids, the hydracids corresponding to the last-enumerated four compounds of silver. Many of the precipitated salts of silver exhibit a peculiar color, (chromate of silver, arseniate of silver,) or manifest a characteristic deportment with other reagents, or upon the application of heat; (formiate of silver); nitrate of

The [illegible] NH_3 + CuO forms a blue compound silver is consequently a very important agent for the direct detection of certain individual acids.

§ 37.

14 PERCHLORIDE OF IRON. ($Fe_2 Cl_3$.)

Preparation.—Heat a mixture of two parts of hydrochloric acid, and from six to eight parts of water, with an excess of small iron nails free from rust, until the evolution of hydrogen ceases; decant the solution into a very capacious vessel, and add one part of hydrochloric acid to the decanted fluid. Heat the mixture to boiling, and drop nitric acid cautiously and gradually into the boiling fluid until the addition of this reagent ceases to produce effervescence of nitric oxide gas, and evolution of nitrous acid fumes, and until a sample of the fluid fails to impart a blue color to a solution of ferricyanide of potassium, (§ 44). A small excess of nitric acid, however, does no harm. Dilute the solution with water, heat to boiling, add ammonia to alkaline reaction, and wash the produced precipitate of hydrated peroxide of iron thoroughly with hot water. Now heat a mixture of two and a half parts of hydrochloric acid with ten parts of water, and project the still moist precipitate gradually into it until the last added particles remain undissolved, even upon continued application of heat. Filter the solution finally, and keep the filtrate for use.

Tests.—Solution of perchloride of iron must not contain an excess of acid; this may be readily ascertained by stirring a sample of it with a glass rod, which has previously been dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate, which shaking of the vessel and agitation of the fluid fail to redissolve. Ferricyanide of potassium must not impart a blue color to it.

Uses.—Perchloride of iron serves to subdivide the group of organic acids which chloride of calcium fails to precipitate, since benzoate and succinate of iron are insoluble, whilst acetate and formiate of iron are soluble. The aqueous solutions of the neutral peracetate and performiate of iron exhibit an intensely red color; perchloride of iron is therefore a useful agent for the detecting acetic acid and formic acid. Perchloride of iron is exceedingly well adapted to effect the decomposition of phosphates of the alkaline earths, vide § 99, *a.*, 8. Finally, this reagent is applied, for the detection of hydroferrocyanic acid, since it produces Prussian blue with this acid.

II. SPECIAL REAGENTS IN THE HUMID WAY.

a. Reagents which serve principally for the detection or separation of individual bases.

§ 38.

1. SULPHATE OF POTASS. ($K O, S O_3$.)

Preparation.—The sulphate of potass of commerce is purified by re-crystallization, and one part of the pure salt is dissolved in twelve parts of water for use.

Uses.—Sulphate of potass precipitates from solutions of salts of barytes and strontia the insoluble sulphates of the oxides. It serves, therefore, to effect the detection and separation of barytes and strontia. It produces likewise a precipitate in very highly concentrated solutions of lime, but, in most cases this precipitate forms only after the lapse of some time; it fails to precipitate dilute solutions of lime. The action of sulphate of potass is analogous to that of dilute sulphuric acid; the former reagent is, however, in many cases preferable to the latter, since it does not disturb the neutrality of the solution.

§ 39.

2. PHOSPHATE OF SODA. (PO_5, 2 Na O, HO.)

Preparation.—Heat dilute phosphoric acid of commerce, and add solution of carbonate of soda until all effervescence ceases, and the fluid begins to manifest an alkaline reaction. Filter the fluid and crystallize the filtrate subsequently by evaporation; purify the produced salt by repeated recrystallization, and dissolve one part of the pure salt in 10 parts of water for use.

Tests.—Solution of phosphate of soda must not become turbid when heated with ammonia. The precipitates which solution of nitrate of barytes and solution of nitrate of silver produce in it, must completely redissolve upon addition of dilute nitric acid.

Uses.—Phosphate of soda precipitates the alkaline earths, and all metallic oxides, by double affinity. It serves in the course of analysis, after the separation of the heavy metallic oxides, as a test for alkaline earths in general; and, after the separation of barytes, strontia, and lime, as a special test for the detection of magnesia, for which latter purpose it is used in conjunction with ammonia, the magnesia precipitating, under these circumstances, as basic phosphate of magnesia and ammonia.

§ 40.

3. ANTIMONIATE OF POTASS. ($KO, Sb\ O_5$.)

Preparation.—Mix four parts of metallic antimony of commerce with nine parts of nitrate of potass; project the mixture gradually into a red-hot hessian crucible, and continue for some time to maintain the latter in a state of ignition. Boil the fused mass subsequently with water until the soluble part is completely extracted; dry the residue, mix 50 parts of it with 24 parts of dry carbonate of potass, introduce the mixture into a hessian crucible, and expose the latter for 30 minutes to red heat; keep the thus produced friable mass in a stoppered phial.—For use, digest one part of the triturated mass with 20 parts of water at a gentle heat, allow the solution to cool, and filter it when quite cold. The solution obtained upon boiling the *antimonium diaphoreticum non ablutum*, (*Phar. Bor.*) may likewise be used, since the salts which this solution contains in admixture scarcely impair the susceptibility of the reaction.

Uses.—Antimonic acid forms with soda a salt of extremely difficult solubility. Antimoniate of potass affords us therefore a means of detecting the presence of soda. Antimonic acid forms, however, insoluble compounds with the alkaline earths, and with most of the metallic oxides. Antimoniate of potass can, therefore, only serve for the detection of soda in cases where the fluid to be analysed contains simply soda or potass. For further particulars on this point, I refer to § 86.

§ 41.

4. NEUTRAL CHROMATE OF POTASS. ($KO, Cr\ O_3$.)

Preparation.—Dissolve the bichromate of potass of commerce in water and add carbonate of potass to feebly alkaline reaction. Crystallize the yellow fluid thus produced; wash the crystals thoroughly, and dissolve one part of the salt in ten parts of water, for use. The solution must be neutral.

Uses.—Chromate of potass decomposes most of the soluble salts with metallic oxides, by double affinity. Most of the precipitated chromates are very difficultly soluble, and many of them exhibit characteristic colours which lead readily to the detection of the individual metal which they respectively contain. We use chromate of potass principally as a test for lead.

§ 42.

5. CYANIDE OF POTASSIUM. ($K\ Cy$.)

Preparation.—A certain portion of ferrocyanide of potassium of commerce is rendered anhydrous by the application of a gentle heat assisted by stirring; the anhydrous mass is levigated, and eight parts of the dry powder are intimately mixed with three parts of perfectly dry carbonate of potass; the mixture is introduced into a red-hot hessian, or, better still, iron crucible, and the latter well covered and maintained at a moderate red heat, until the mixture is in a state of clear and calm fusion. The fused cyanide of potassium is then poured into a heated porcelain or silver basin, or upon a clean iron plate; this part of the process must be executed with great care and caution to prevent the passing over of any of the minute particles of iron which have separated in the process of fusion, and subsided to the bottom of the crucible. The cyanide of potassium thus obtained is exceedingly well adapted for analytical purposes, although it contains an admixture of cyanate of potass which, upon solution in water, is transformed into carbonate of ammonia, and carbonate of potass, ($KO, NC_2 O + 4 HO = KO, CO_2 + NH_4 O, CO_2$). The *real* formula for this cyanide of potassium is accordingly $= 5 K Cy + KO, Cy O$.—For use, one part of it is dissolved in four parts of distilled water, without application of heat.

Tests.—Cyanide of potassium must be of a milk white color, and perfectly free from any admixture of particles of iron. The solution in water should be perfectly clear. It ought to contain neither silicic acid nor sulphuret of potassium; the precipitate which salts of lead produce in its solution, must exhibit a pure white appearance, and the residue which its solution leaves upon evaporation after previous supersaturation with hydrochloric acid must yield a perfectly clear solution when treated with water.

Uses.—Cyanide of potassium (containing an admixture of cyanate of potass) produces in the solutions of most of the salts with metallic oxides, precipitates of metallic cyanides, oxides or carbonates, which are insoluble in water. The precipitated cyanides are soluble in cyanide of potassium, and may therefore be separated from the oxides or carbonates, by further addition of this reagent. Some of the metallic cyanides redissolve invariably in conjunction with the cyanide of potassium as double cyanides, even in presence of free hydrocyanic acid; whilst the metals of others combine with cyanogen, giving rise to the formation of new radicals, which are thus obtained in solution in combination with potassium. The most common compounds of the latter description are cobalto-cyanide of potassium, and ferro and ferricyanide of potassium. These differ from the double cyanides of the former description, particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may consequently serve to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in cyanide of potassium. In the course of analysis, this reagent serves to effect the separation of cobalt from nickel, and also of copper from cadmium. (Compare § 89 and § 92.)

§ 43.

6. FERROCYANIDE OF POTASSIUM. ($C_6 N_3 Fe + 2 K = Cfy + 2 K$.)

Preparation.—Ferrocyanide of potassium of commerce is sufficiently pure for the purposes of chemical analysis. One part of the salt is dissolved in twelve parts of water, for use.

Uses.—Ferrocyanogen forms with most metals compounds, insoluble in water, and which frequently exhibit highly characteristic colors. These ferrocyanides are formed when ferrocyanide of potassium is brought into contact with soluble salts of metallic oxides, with chlorides, &c., the potassium changing place with the metals. Ferrocyanide of copper and perferrocyanide of iron exhibit the most characteristic colors of all, and ferrocyanide of potassium serves, therefore, particularly as a test for copper and peroxide of iron.

§ 44.

7. FERRICYANIDE OF POTASSIUM.

($C_{12} N_6 Fe_2 + 3 K = 2 Cfy + 3 K$.)

Preparation.—This reagent is produced by transmitting chlorine gas through a solution of one part of ferrocyanide of potassium in ten parts of water, until the addition of a few drops of the fluid fails to produce a blue precipitate or color in a solution of perchloride of iron. The solution is then concentrated by evaporation, and some carbonate of potass added, until the mixture begins to manifest a feebly-alkaline reaction. The liquid is then filtered, and the filtrate allowed to cool. The crystals obtained are of a magnificent red color. One part of the salt is dissolved in ten parts of water, for use. The solution, as already remarked, must neither produce a blue precipitate nor a blue color, when added to solution of perchloride of iron.

Uses.—Ferricyanide of potassium decomposes with solutions of metallic oxides, in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides, that of iron is more particularly characterized by its color, and we apply ferricianide of potassium, therefore, principally as a test for protoxide of iron. Ferricyanide of potassium intended for this purpose may very well be prepared extempore, by gradually adding nitric acid to a solution of ferrocyanide of potassium, until a sample of the mixture ceases to impart a blue color to solution of perchloride of iron. All elevation of temperature must be avoided in this process, and the vessel ought to be agitated whilst the nitric acid is added.

§ 45.

8. SULPHOCYANIDE OF POTASSIUM. ($2\,CyS + K.$)

Preparation.—Mix intimately forty-six parts of anhydrous ferrocyanide of potassium, seventeen parts of carbonate of potass, and thirty-two parts of sulphur; introduce the mixture into an iron pan provided with a lid, and heat to fusion at a gentle fire; maintain the same moderate heat until the turgescence of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; increase the temperature now, towards the end of the operation, to faint redness, in order to decompose the hyposulphite of potass which has been formed in this process. Remove the half-refrigerated and still soft mass from the pan, break or crush it, and boil the pieces with alcohol. From the thus produced alcoholic solution, part of the sulphocyanide of potassium will separate in colorless crystals, upon cooling; the rest may be obtained by distilling the alcohol off from the mother liquor. One part of the salt is dissolved in ten parts of water, for use.

Uses.—Sulphocyanide of potassium serves for the detection of peroxide of iron, the presence of which it indicates with the greatest possible susceptibility and precision; it is in this respect preferable to all other reagents.

§ 46.

9. HYDROFLUOSILICIC ACID. ($Si\,Fl_2$, $Fl\,H$.)

Preparation.—A mixture of one part of sand and one part of fluor-spar powder is introduced into a glass flask, and six parts of sulphuric acid poured over it; the aperture of the flask is closed with a perforated cork, into which the one end of a bent tube is fitted air-tight. The other limb of the tube is made to pass to the bottom of a tall flat-bottomed glass jar, into which a small amount of mercury is poured sufficient to cover the extremity of the tube to the extent of several lines; the mercury is then covered with four parts of water. The disengagement of fluosilicic gas, which commences even in the cold, is promoted by exposing the flask to a gentle heat, in the sand-bath. Every gas bubble ascending through the mercury produces in the water a precipitate of hydrated silicic acid. The rationale of this process is, that of every three equivalents of fluoride of silicon, ($Si\,Fl_2$), one equivalent transposes with two equivalents of water into silicic acid ($Si\,O_2$), which separates, and hydrofluoric acid which combines with the two undecomposed equivalents of fluoride of silicon to hydrofluosilicic acid.

$$[3\,Si\,Fl_2 + 2\,H\,O = 2\,(Si\,Fl_2,\,Fl\,H) + Si\,O_2.]$$

The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the exit tube must be placed under mercury, since it would speedily be choked if this precaution were neglected. It sometimes happens in the course, and especially towards the end, of the operation, that the gas forms complete tubes or channels of silica in the gelatinous liquid, through which it subsequently gains the surface without undergoing decomposition, if they are not occasionally broken by stirring the liquid. When the evolution of gas has completely ceased, the gelatinous paste is thrown upon a piece of linen, and the fluid squeezed through and subsequently passed through a filter. The filtrate is kept for use.

Tests.—Hydrofluosilicic acid, mixed with two parts of water, must produce no precipitate in solutions of salts of strontia.

Uses.—Bases transpose with hydrofluosilicic acid, into water, and metallic silicofluorides. Many of the latter are soluble, whilst others are insoluble; the latter may, therefore, by means of this reagent, be distinguished from the former. In the course of analysis, hydrofluosilicic acid is applied simply for the detection of barytes.

§ 47.

10. Oxalic acid. ($2\,CO + O = C_2\,O_3 = \bar{O}$.)

Preparation.—Pour a mixture of 5 parts of nitric acid of 1.42 spec. grav., and 10 parts of water, over one part of starch in a porcelain basin, and heat gently until the evolution of nitrous acid ceases. Filter the fluid, and bring the filtrate to crystallization; drain the mother liquor off, and purify the crystals subsequently by recrystallization. Keep the produced substances in powder, since its solution speedily suffers decomposition.

Tests.—Oxalic acid, when boiled with a small amount of indigo solution, must not discolor the latter.

Uses.—Oxalic acid forms with many bases, salts which are insoluble in water, and therefore serves to effect the precipitation of such bases. Many of these insoluble oxalates are readily soluble in an excess of oxalic acid, whilst others dissolve with difficulty in the same menstruum;—this different deportment distinguishes the precipitated bases from one another. But since all the oxalates which are insoluble in water, dissolve in stronger acids, (hydrochloric acid, and nitric acid,) oxalic acid will in most cases effect the complete precipitation of the respective bases only if the liberated acid is saturated with an alkali.

In the systematic course of analysis, oxalic acid is a very valuable and important agent for the detection and separation of lime.

§ 48.

11. OXALATE OF AMMONIA. ($N\,H_4\,O, \bar{O}$.)

Preparation.—Dissolve oxalic acid in water, add ammonia until the fluid begins to manifest a feebly alkaline reaction, and crystallize. Dissolve one part of the salt in 24 parts of water, for use.

Uses.—Oxalate of ammonia is very conveniently substituted for oxalic acid and ammonia. It has this great advantage over free oxalic acid, that its solution keeps, whilst that of the free acid suffers decomposition.

§ 49.

12. TARTARIC ACID. ($C_4 H_2 O_5 = \overline{T}$.)

The tartaric acid of commerce is sufficiently pure for the purpose of chemical analysis. It is best preserved in powder, since its solution, after some time, suffers decomposition, attended with the formation of a white film upon its surface.

Uses.—The addition of tartaric acid to a solution of iron, manganese, chromium, alumina, cobalt, and various other metals, prevents the usual precipitation of these metals upon the subsequent addition of an alkali : their non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may serve accordingly to effect the separation of these metals from those the precipitation of which it fails to prevent. Tartaric acid forms a difficultly soluble acid or bisalt with potass, but not so with soda ; it is therefore one of our best reagents to distinguish potass from soda.

§ 50.

13. CAUSTIC BARYTES. (BaO.)

Preparation.—Boil one part of sulphuret of barium (§ 33) with 20 parts of water ; add to the hot solution an excess of pulverized copper scales, and apply heat until a filtered sample of the fluid fails to impart a black color to a solution of acetate of lead. Filter the fluid whilst hot, and add a sufficient amount of water to prevent the subsequent crystallization—(upon cooling)—of any considerable portion of the dissolved hydrate of barytes. Keep the saturated water of barytes in well-stoppered phials ;

should it contain an admixture of copper, this may be readily removed by cautiously adding sulphuretted hydrogen, and filtering the fluid subsequently off from the precipitated sulphuret of copper.

Uses.—Caustic barytes is a strong base, and acts analogously to lime, i. e. it precipitates the alkaline earths and metallic oxides which are insoluble in water, from the solution of their salts. We use barytes in the course of analysis, simply for the precipitation of magnesia, and for this purpose solution of sulphuret of barium will serve as well, provided it contain an admixture of caustic barytes.* Water of barytes may serve, moreover, like chloride of barium and nitrate of barytes, to effect the precipitation of those acids which form insoluble compounds with barytes; in this respect, however, water of barytes is principally applied only for the detection of carbonic acid.

§ 51.

14. PROTOCHLORIDE OF TIN. (Sn Cl.)

Preparation.—Fuse a certain amount of English tin in an iron spoon, and, after having removed the latter from the fire, triturate the fused mass with a pestle until it has completely solidified. Introduce the powder which is thus obtained, into a flask, pour concentrated sulphuric acid over it, (taking care, always, that the tin predominate,) and boil the mixture; dilute the solution subsequently with four times its amount of water, slightly acidulated with hydrochloric acid, and filter. Pour the filtrate into a phial containing small fragments of metallic tin, and close the phial carefully. If these precautions be neglected, the protochloride will soon change into perchloride, which, of course, will render the reagent totally unfit for the purposes for which it is intended.

Tests.—Solution of protochloride of tin, when added to a solution of perchloride of mercury, must immediately produce a white precipitate of protochloride of mercury; when treated with sulphuretted hydrogen, it must yield a dark brown precipitate; it should not be precipitated, nor rendered turbid by sulphuric acid.

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* Sulphuret of barium contains invariably an admixture of caustic barytes, when not prepared at an *exceedingly* high temperature.

Uses.—The great tendency of protochloride of tin to absorb oxygen, and thus to form peroxide,—or rather perchloride of tin, since the peroxide, in the moment of its formation, transposes with the free hydrochloric acid present,—render this substance one of our most powerful reducing agents. We use this reagent, in the course of analysis, as a test for mercury, and likewise to effect the detection of gold, for which latter purpose it is previously to be mixed with some nitric acid without heating.

§ 52.

15. PERCHLORIDE OF GOLD. ($Au Cl_3$.)

Preparation.—To produce this reagent, fine shreds of gold, which may be alloyed either with silver or copper, are introduced into a flask, and drenched with an excess of aqua regia; a gentle heat is then applied to the flask, and maintained as long as the metallic mass continues to dissolve. A sample of the solution is then diluted with water, and subsequently tested with ferrocyanide of potassium; should this reagent produce a brown red precipitate, this is a sure sign that the gold was alloyed with copper, and the solution is, in that case, to be mixed with solution of protosulphate of iron in excess, when the perchloride of gold will suffer reduction to the metallic state, the gold separating in form of a fine brownish black powder; the latter is then introduced into a small flask, thoroughly washed, and subsequently redissolved in aqua regia; the solution is evaporated to dryness in the water-bath, and the residue finally dissolved in thirty parts of water. Should the gold be alloyed with silver, the latter metal will at once remain as chloride of silver, upon treating the alloy with aqua regia. In this case, the solution is to be at once evaporated to dryness, and the residue dissolved for use in thirty parts of water.

Uses.—Perchloride of gold has a great tendency to yield up its chlorine to other substances, and accordingly possesses the property of converting protochlorides into perchlorides, protoxides into peroxides and perchlorides, &c. These peroxidations, &c. are usually indicated by the precipitation of pure metallic gold, in form of a blackish brown powder. In the systematic course of analysis, this reagent serves exclusively for the detection of protoxide of tin, in the solution of which it produces a purple color, or a purple-colored precipitate. (Vide infra.)

§ 53.

16. BICHLORIDE OF PLATINUM. ($Pt\,Cl_2$.)

Preparation.—To obtain this reagent, platinum filings, which have been purified previously by boiling with nitric acid, are introduced into a narrow-necked flask, and drenched with concentrated hydrochloric acid; some nitric acid is then added, and a gentle heat applied, with occasional additions of fresh portions of nitric acid; this process is continued until the platinum is completely dissolved. The solution is subsequently evaporated to dryness in the water-bath, some hydrochloric acid being added during the operation; the residue is finally dissolved in ten parts of water.

Uses.—Perchloride of platinum forms very sparingly soluble double salts, with chloride of potassium and chloride of ammonium, whilst the double salt which it forms with chloride of sodium is very readily soluble. It serves, therefore, to detect ammonia and potass, and is, indeed, our most susceptible reagent for the latter substance.

§ 54.

17. ZINC. (Zn.)

Pure sublimed zinc is selected for the purposes of chemical analysis; particular care should be taken to have it perfectly free from arsenic. The method described at § 25 will serve to detect the presence of the slightest trace of this substance. The pure sublimed zinc is to be fused, and a portion of it gradually dropped into a large vessel, containing water; the remainder is to be cast into small cylinders, by pouring the fused metal into wooden moulds, coated with chalk.

Uses.—The great affinity which zinc possesses for oxygen and its oxides for acids, renders this metal a very valuable agent to effect the reduction of many metallic salts and oxides, and consequent precipitation of the reduced metals. Since the thus precipitated metals vary in color, form, &c., this reagent may likewise serve for their individual detection. We apply it principally for the precipitation of antimony and of tin. Zinc is moreover frequently used for the evolution of hydrogen.

§ 55.

18. IRON. (Fe.)

Iron, like zinc, reduces many metallic salts and oxides, and precipitates the reduced metals. We use it especially for the detection of copper, which precipitates upon it with its characteristic color. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, &c., will serve for this purpose.

§ 56.

19. COPPER. (Cu.)

We use copper exclusively to effect the reduction of mercurial salts; the metallic mercury precipitates upon the surface of the copper, forming a white coating, which shines with silvery lustre when rubbed. Any copper coin scoured with fine sand, in fact any clean surface of copper, may be employed for this purpose.

b. Special reagents, which are principally applied for the detection or separation of individual acids.

§ 57.

1. ACETATE OF POTASS. (K O, $\bar{A}$.)

Preparation.—This reagent is prepared by dissolving one part of pure carbonate of potass in two parts of water, heating the solution, and saturating it *exactly* with acetic acid. Acetate of potass being but rarely required in analysis, it is best to prepare it fresh every time that it is needed.

Uses.—Any of the salts of potass may serve to produce a precipitate of tartar, and therefore to detect tartaric acid; but the acetate of potass is peculiarly adapted for this purpose, since the precipitated bitartrate of potass is insoluble in the liberated acetic acid. Acetate of potass serves also to precipitate from simple solutions in free mineral acids, certain compounds which are insoluble in acetic acid. In the systematic course of analysis it is principally applied in the process of the decomposition of the phosphated alkaline earths, to effect the precipitation of the perphosphate of iron from hydrochloric solution.

§ 58.

2. CAUSTIC LIME. ($Ca\ O.$)

Preparation.—Take recently prepared hydrate of lime, and digest it for some time with cold, distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, and decant subsequently, and keep the clear fluid in well-stoppered phials. Besides lime-water, hydrate of lime should also be kept in store.

Tests.—Lime-water must impart a strongly-pronounced brown tint to turmeric paper, and yield with carbonate of potass a not too inconsiderable precipitate. It is totally unfit for use as soon as it loses these properties, which happens speedily when it is exposed to the contact of air.

Uses.—Lime forms with many acids insoluble, with others soluble salts. Lime-water may accordingly serve to distinguish the former acids, which it precipitates from the latter, which it fails to precipitate. Many of the precipitated acids precipitate only under certain conditions, e. g. on boiling, (citric acid,) and it is therefore easy to distinguish them from one another individually by altering these conditions. We employ lime-water principally to effect the detection of carbonic acid, and also to distinguish paratartaric acid, tartaric acid, and citric acid, from one another.—Hydrate of lime serves, like caustic potass, to liberate ammonia, and is in many cases preferable to the latter reagent.

§ 59.

3. SULPHATE OF LIME. ($Ca\,O, S\,O_3$.)

Preparation.—To produce this reagent, a concentrated solution of chloride of calcium is mixed with dilute sulphuric acid, the precipitate produced is thoroughly washed, digested, and agitated for some time with water; the undissolved particles are then allowed to subside, and the clear supernatant fluid is decanted and kept for use.

Uses.—Sulphate of lime serves to effect the further subdivision of those acids which are precipitable by chloride of calcium, since, owing to its difficult solubility, a few acids only of that group (oxalic acid, paratartaric acid,) produce precipitates in its solution. The solution of sulphate of lime serves moreover as a reagent for bases, viz. to distinguish and separate barytes, strontia, and lime from one another, since, of course, it fails to precipitate the latter, whilst it acts upon solutions of barytes and strontia in the same manner as highly dilute sulphuric acid, i. e. it precipitates the barytes immediately, and the strontia only after the lapse of some time.

§ 60.

4. CHLORIDE OF MAGNESIUM. ($Mg\,Cl$.)

Preparation.—Chloride of magnesium is prepared by heating a mixture of one part of hydrochloric acid and two and a half parts of water, and adding basic carbonate of magnesia, (magnesiæ carbonas of the shops,) until the liquid ceases to manifest acid reaction. The solution is then once more boiled up, subsequently filtered, and kept for use. Sulphate of magnesia may, in most cases, be substituted for chloride of magnesium.

Uses.—Chloride of magnesium serves almost exclusively for the detection of phosphoric acid, which it precipitates from aqueous solutions of phosphates, in presence of ammonia, in the form of a double salt, (basic phosphate of magnesia and ammonia,) which is nearly insoluble, and possessed of highly characteristic properties. Chloride of magnesium is moreover applied to test the purity of hydrosulphuret of ammonia. (Vide § 27.)

§ 61.

5. PROTOSULPHATE OF IRON. ($Fe\,O, S\,O_3$.)

Preparation.—To prepare this reagent, iron nails in excess, free from rust, are heated with dilute sulphuric acid until the evolution of hydrogen ceases; the solution is then filtered, and a few drops of dilute sulphuric acid are added to the filtrate, which is subsequently allowed to cool. A sufficiently concentrated solution will yield crystals simply upon cooling; dilute solutions require evaporation for the production of crystals. The crystals are washed with water slightly acidulated with sulphuric acid, and are subsequently dried and preserved.

Uses.—Protosulphate of iron has a great disposition to absorb oxygen and to be converted into persulphate of iron. It acts therefore as a powerful reducing agent. We employ it principally to effect the reduction of nitric acid, which it reduces to the state of nitric oxide by withdrawing three atoms of oxygen from it. The reduction of the nitric acid being attended, in this case, with the formation of a very peculiar, intensely brownish-black compound of nitric oxide with undecomposed protosulphate of iron, this reaction is particularly characteristic and susceptible for the detection of nitric acid. Protosulphate of iron serves moreover for the detection of hydro-ferricyanic acid, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of the salts of this metal.

§ 62.

6. SOLUTION OF MAGNETIC OXIDE OF IRON (FERROSO-FERRIC OXIDE.)

$Fe\,O, SO_3 + Fe_2\,Cl_3$.)

This reagent is not kept on hand, but prepared, when needed, by mixing solution of protosulphate of iron with some perchloride of iron. It serves for the detection of hydrocyanic acid, which when previously combined with alkalies, yields with it a precipitate of sesquiferrocyanide of iron. (Prussian blue).

63.

7. PROTOXIDE OF LEAD. ($\mathrm{Pb\,O}$.)

Protoxide of lead is employed for the detection of free acetic acid, since it forms with this acid alone, a soluble compound, possessed of alkaline reaction. Finely-elutriated litharge answers this purpose sufficiently well. (Compare § 105, *a.*, 7.)

§ 64.

8. NEUTRAL ACETATE OF LEAD. ($\mathrm{Pb\,O}, \bar{\mathrm{A}}$.)

The better sorts of commercial acetate of lead are sufficiently pure for the purposes of chemical analysis. One part of the salt is dissolved in ten parts of water for use.

Uses.—Protoxide of lead forms with a great many acids, compounds which are insoluble in water, and marked either by their peculiar color or characteristic deportment. The acetate of lead for instance, produces precipitates in the solutions of these acids or of their salts, and contributes essentially to detect and distinguish several of them individually. Thus, in particular, chromate of lead is characterised by its yellow color, phosphate of lead by its peculiar deportment before the blow-pipe, and malate of lead by its ready fusibility.

§ 65.

9. BASIC ACETATE OF LEAD. ($3\,\mathrm{Pb\,O}, \bar{\mathrm{A}}$.)

Preparation.—Introduce a mixture of seven parts of finely elutriated litharge with six parts of neutral acetate of lead into a flask, and pour thirty parts of water over it; close the flask carefully, and allow it to stand in a moderately warm spot, with occasional agitation of its contents, until the sediment in it is perfectly white. Decant subsequently, and keep the clear fluid in a well-stoppered phial. This reagent is unfit for use, if it contains the slightest admixture of copper; it is necessary, therefore, to test it with ammonia; should it acquire a blue color upon the addition of this reagent, this is a sure sign of the presence of copper, which is to be removed, in such cases, by digesting the solution with metallic lead until all the copper is precipitated.

Uses.—The basic acetate of lead, like the neutral acetate, precipitates those acids which form insoluble compounds with oxide of lead, and indeed all those which are soluble in acetic acid, more completely than the former reagent. We employ it in analysis especially for the detection of sulphuretted hydrogen, for which substance it is our most susceptible reagent. It serves, moreover, to neutralize free acids, in cases where it is desirable to avoid the application of an alkali, thus it is used, for instance, to render highly acid solutions of nitrate of bismuth precipitable by water.

§ 66.

10. HYDRATED OXIDE OF BISMUTH. $(\mathrm{Bi\,O + H\,O.})$

Preparation.—Coarsely-pounded bismuth is gradually projected into pure nitric acid of 1.2 sp. gr. as long as it continues to dissolve in the acid; the operation is to be assisted by the application of a gentle heat. The solution is diluted with about an equal quantity of warm water, (slightly acidified with nitric acid,) and subsequently filtered; the filtrate is mixed with from ten to twenty parts of water, and ammonia added to the milky fluid, until it predominates perceptibly; the mixture is then heated, and the precipitate which has formed in it is subsequently washed, first by decantation, and finally upon a filter; the washed precipitate is afterwards dried between some sheets of blotting-paper, at a moderate heat.

Uses.—The oxide of bismuth, when boiled with alkaline solutions, of metallic sulphurets, transposes with the latter, giving thus rise to the formation of metallic oxides, and sulphuret of bismuth. It is better adapted for this purpose than oxide of copper, since it enables the operator to judge immediately upon the addition of a fresh portion whether the decomposition is completed or not. It has still another advantage over oxide of copper, viz., it does not, like the latter, dissolve in the alkaline fluid, in presence of organic substances, nor does it act as a reducing agent upon reducible oxygen compounds. We use the hydrated oxide of bismuth principally to convert sulpharsenious and sulphuric acid into arsenious and arsenic acid, for which purpose oxide of copper is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of sub-oxide

§ 67.

11. SULPHATE OF COPPER. (CuO, SO_3.)

Preparation.—The blue vitriol of commerce, purified by recrystallization, is perfectly well adapted for the purposes of chemical analysis.

Uses.—Sulphate of copper is employed in qualitative analysis, to effect the precipitation of hydriodic acid as protiodide of copper. For this purpose it is necessary to mix the solution of one part of the blue vitriol with two parts and a quarter of protosulphate of iron, otherwise half of the iodine will separate in a free state. The protoxide of iron is peroxidized in this process at the expense of the oxygen of the oxide of copper, which latter is thus reduced to the state of suboxide. Sulphate of copper is used, moreover, as a test for arsenious and arsenic acid, and it is indeed in this respect a very *susceptible,* but by no means a *characteristic* reagent. For this purpose it is best to convert the sulphate into ammonio-sulphate of copper by adding to its solution until the precipitate which forms at first, is just redissolved. Sulphate of copper, applied in conjunction with potass, is however a most excellent means to distinguish arsenious acid from arsenic acid, since the presence of the former acid is indicated at once by the separation of red oxide (suboxide) of copper. Compare § 95, *d.*, 7. Sulphate of copper may also serve to detect the presence of hydroferrocyanic acid.

§ 68.

12. PROTONITRATE OF MERCURY. ($Hg_2 O, NO_5$.)

Preparation.—To prepare this reagent, nine parts of nitric acid, of 1.23 sp. gr., are gently heated in a small flask, in conjunction with ten parts of mercury, until the disengagement of nitrous acid fumes ceases; the solution is then boiled for some time with the undissolved portion of the mercury, taking care to replace the evaporating water, and this process is continued until the whole of the mercury contained in a sample of the fluid is precipitated as protochloride, upon the addition of a solution of common salt in excess, so that protochloride of zinc fails to produce the slightest precipitate in the liquid filtered off from the precipitated protochloride. The solution is then agitated with the undissolved mercury until cold; the crystals obtained are pounded, and subsequently agitated with twenty parts of cold water, slightly acidulated with nitric acid. The fluid is then filtered, if necessary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

Uses.—The protonitrate of mercury acts in an analogous manner to the corresponding salt of silver. In the first place, it precipitates many acids, especially the hydracids; and secondly, it serves for the detection of several readily oxidizable substances, e. g. of formic acid, since the oxidation of such substances, at the expense of the oxygen of the black oxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 69.

13. PEROXIDE OF MERCURY. ($Hg O$.)

The peroxide of mercury of commerce is very finely levigated, previously to which the peroxide of mercury should be moistened with some alcohol to prevent its minute particles from rising into the air. The powder is kept for use. Peroxide of mercury is a safe and characteristic reagent for hydrocyanic acid, since it dissolves in alkaline fluids only when this acid is present. (Compare § 101, *d.*, 5.)

§ 70.

14. PERCHLORIDE OF MERCURY. ($Hg\,Cl.$)

The commercial perchloride of mercury is sufficiently pure for the purposes of chemical analysis. For use, one part of the salt is dissolved in sixteen parts of water.

Uses.—Perchloride of mercury yields with various acids, e. g. with hydriodic acid, precipitates of characteristic color, but it is, nevertheless, one of the least essential reagents for the determination of individual acids. It serves also as an oxidizing agent, and enables us to detect the presence of readily oxidizable bodies, e. g. of protoxide of tin, by the precipitation of protochloride of mercury, attendant upon their oxidation.

§ 71.

AMMONIO-NITRATE OF SILVER. ($Ag\,O, NO_5 + 2\,N\,H_3.$)

This reagent is not kept on hand, but prepared fresh every time when needed for use; its preparation is very simple: caustic ammonia is cautiously dropped into a solution of nitrate of silver, till the precipitate which forms at first is redissolved. It serves for the detection of arsenious and arsenic acid in solutions which contain a free acid.

§ 72.

16. SULPHUROUS ACID. ($S\,O_2.$)

Preparation.—Introduce a certain amount of small pieces of charcoal into a flask, add from six to eight times their weight of sulphuric acid, apply heat, and conduct the evolved gas into cold water, taking care to keep the receiver cool; continue the process until the water ceases to absorb sulphurous acid. The solution thus obtained must be kept in well-stoppered phials.

Uses.—Sulphurous acid has a great tendency to absorb oxygen and to be thus converted into sulphuric acid. It is, therefore, one of our most powerful reducing agents, and effects the precipitation of metallic mercury from solutions of mercurial salts, and the reduction of chromic acid to oxide of chromium, as protochloride of tin does. We employ sulphurous acid principally to convert arsenic acid into arsenious acid, as a preliminary and greatly facilitating step towards the subsequent precipitation of the arsenic by means of sulphuretted hydrogen, (vide § 95, *e.*, 3.) Before applying this reagent, it is always necessary to ascertain by the smell whether it continues perfectly fit for use.

§ 73.

17. CHLORINE. (Cl.)

Preparation.—Introduce one part of peroxide of manganese in powder into a flask, and add from four to five parts of commercial hydrochloric acid; apply a gentle heat to the flask, and conduct the evolved gas into a jar containing from thirty to forty parts of water of the lowest possible temperature. Keep the thus produced chlorine water in a well-closed bottle, cautiously protected from the influence of light, since if this precaution be neglected, the reagent will soon become completely decomposed, i. e. converted into dilute hydrochloric acid, with evolution of oxygen, (owing to the decomposition of the water.)

Uses.—Chlorine has a greater affinity for metals and for hydrogen than iodine and bromine. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. Free chlorine forming with bromine, chloride of bromine, and with iodine, chloride of iodine, and these compounds presenting a different deportment from that of the free metalloids, the greatest care must be taken, in certain cases, e. g. when testing for iodine by means of starch, (§ 101, *c.*, 8), to avoid adding chlorine water in excess. Chlorine serves, moreover, for the destruction of organic substances, by withdrawing hydrogen from the water, which contains these substances, so that the liberated oxygen is enabled to combine with the vegetable matter, and thus to effect their decomposition. For this latter purpose it is most advisable to *evolve* the chlorine in the fluid, which contains the organic substances; this is effected by adding hydrochloric acid to the fluid, heating the mixture to boiling, and adding, finally, chlorate of potash. This gives rise to the formation of chloride of potassium and water, and to the disengagement of chloroso-chloric acid, (Cl_3 O_{13}, MILLON), which acid acts analogously to chlorine.

§ 74.

18. SOLUTION OF INDIGO.

Preparation.—One part of indigo powder is heated with seven parts of fuming sulphuric acid. For use, the solution obtained is diluted, with so much water that the fluid appears just still distinctly blue.

Uses.—Indigo is decomposed upon boiling with nitric acid, and this decomposition is attended with the formation of oxidation-products of a yellow color. Solution of indigo serves therefore for the detection of nitric acid, both in a free state and in nitrates, in which latter, however, the nitric acid must first be liberated by means of sulphuric acid.

§ 75.

19. STARCH-PASTE.

Common starch is rubbed with cold water, and the mixture subsequently heated to boiling, with constant stirring. The paste must be uniform, and so thin as almost to run.

Uses.—Starch, when brought into contact with free iodine, forms with the latter substance a peculiar dark-blue compound, the color of which is so intense that it remains still distinctly perceptible, even though the two substances be brought together, in a highly dilute state. Starch-paste is therefore a most excellent and delicate test for free iodine. It is far less susceptible with regard to bromine, the fiery yellow color of bromide of starch being not by any means so characteristic and intense as the blue of iodide of starch.

B. REAGENTS IN THE DRY WAY.

1. *Fluxes and decomposing agents.*

§ 76.

1. MIXTURE OF CARBONATE OF SODA AND CARBONATE OF POTASS.

$(NaO, CO_2 + KO, CO_2.)$

Preparation.—Ten parts of effloresced carbonate of soda are intimately mixed (by trituration) with thirteen parts of dry carbonate of potass; the mixture is kept in a closed vessel.

Uses.—When silicic acid or silicates are fused with about four parts, (and consequently with an excess,) of carbonate of potass or soda, carbonic acid escapes with effervescence, and alkaline silicate is formed, which, being soluble in water, may be a basic readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate hydrochloric acid separates the silicic acid invariably in its soluble modification.—When a fixed alkaline carbonate is fused in conjunction with sulphate of barytes, of strontia, or of lime, the carbonic acid transposes with the sulphuric acid; this transposition causes the formation of an alkaline sulphate and carbonate of barytes, strontia, or lime; in these new compounds, both the acid and base of the previously insoluble sulphate may now be readily detected and determined. We use neither carbonate of potass alone nor carbonate of soda alone, to effect the decomposition of the insoluble silicates and sulphates; but we apply for this purpose the above described mixture of both, because this mixture requires a far lower degree of heat for fusion than either of its two components, and thus enables us to conduct the operation over a BERZELIUS' lamp. The fusion with alkaline carbonates is invariably effected in a platinum crucible, provided no reducible metallic oxides be present.

§ 77.

HYDRATE OF BARYTES. $(BaO, HO.)$

Preparation.—The crystals of barytes, prepared according to the directions given at § 50, are heated gently in a porcelain crucible until the crystallization water is completely expelled. The residuary white mass is levigated, and kept for use in a well-closed phial.

Uses.—Hydrate of barytes fuses at a gentle red-heat without losing its water. Upon fusing silicates in conjunction with about four times as much hydrate of barytes, transposition ensues, superbasic silicate of barytes is formed, and the oxides are liberated. Now, upon treating the fused mass subsequently with hydrochloric acid, evaporating the solution to dryness, and digesting the residue with hydrochloric acid, the silicic acid is separated, and the oxides are obtained in solution in the form of chlorides. We use hydrate of barytes as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to the carbonate or nitrate of barytes, since it does not require a very high temperature for its fusion, as is the case with the one of the latter compounds of barytes, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the other. Fluxing with hydrate of barytes is effected in silver or platinum crucibles.

§ 78.

3. NITRATE OF POTASS. ($K O, N O_5$.)

Preparation.—Dissolve commercial nitre in boiling water to complete saturation; dilute the solution subsequently with a small portion of water, filter hot into a beaker-glass, place the latter in cold water, and stir the solution till cold. Project the crystalline powder obtained upon a filter, and wash it with cold water until the rinsings cease to be rendered turbid by nitrate of silver. Dry the washed nitrate of potass well, and keep it for use.

Tests.—A solution of nitrate of potass must neither be rendered turbid by solution of nitrate of silver or nitrate of barytes, nor ought it to be precipitated by carbonate of potass.

Uses.—Nitrate of potass serves as a very powerful oxidizing agent, by yielding oxygen to combustible substances when heated in conjunction with the latter. We use this reagent principally to convert several metallic sulphurets, and more particularly the sulphurets of tin, antimony, and arsenic, into oxides and acids. We use nitrate of potass also to effect the rapid and complete combustion of organic substances; for the latter purpose, however, nitrate of ammonia is preferable in most cases; this reagent is prepared by saturating nitric acid with carbonate of ammonia.

II. Blow-pipe reagents.

§ 79.

1. CHARCOAL. (C.)

Any kind of thoroughly calcined wood-charcoal may be used for blow-pipe experiments. The charcoal of pine or linden-wood is however preferable to any other sort. Smooth pieces ought to be selected, as knotty pieces split when heated, and thus throw off portions of the matter under examination.

Uses.—Charcoal is principally used, in blow-pipe experiments, as a support for the substance under examination, (vide § 13.) The following are the properties which render it so valuable in this respect. First, its infusibility; 2nd, its low conducting power for heat, which admits of substances being heated more strongly upon a charcoal than upon any other support; 3rd, its porosity, by means of which it imbibes readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on its surface; 4th, its property to reduce oxidized bodies, whereby it co-operates in the reduction of oxides by the inner flame of the blow-pipe.—Charcoal serves, moreover, to effect the reduction of arsenious acid and of arsenic acid, since, at a red-heat, it withdraws the oxygen from their acids. For this purpose, the charcoal is used either in the form of small splinters, or as a coarse powder. The separation of the arsenic from its acids requires sometimes the conjoint application of charcoal and an alkaline carbonate; in such cases it is best to use a mixture of effloresced carbonate of soda and lamp-black; this mixture is to be ignited in a covered crucible, and kept in a well-stoppered phial.

§ 80.

2. CARBONATE OF SODA. (NaO, CO_2.)

Preparation.—An intimate mixture of one part of crystallized and three parts of effloresced carbonate of soda is introduced into the broken-off neck of a retort, or into a wide glass tube, or some other vessel of that description; the one aperture of the tube &c. is left open, the other is closed with a perforated cork into which a tube is fitted; this tube is connected with a gas evolution flask containing carbonate of lime, from which carbonic acid is subsequently evolved by means of hydrochloric acid as soon as the whole apparatus is fully prepared. The evolved carbonic acid combines with the carbonate of soda, and forms bicarbonate. The complete saturation of the carbonate of soda with carbonic acid is indicated by the fall of the temperature of the mixture which had become elevated in the course of the process, and by the immediate extinction of an ignited wood-splint, when held before the open aperture of the tube. The salt is now placed upon a filter, and washed with cold water, until the rinsings cease to be rendered turbid by chloride of barium or nitrate of silver, after previous supersaturation with nitric acid; the salt is then dried, and subsequently ignited in a silver, platinum, or porcelain crucible. The ignition of the bicarbonate causes the expulsion of one atom of carbonic acid, and then remains, consequently, simple carbonate of soda. The purity of carbonate of soda is tested by the same means as that of carbonate of potash. Hydrosulphuret of ammonia must not alter its solution.

Uses.—Carbonate of soda is readily fusible, and is, therefore, peculiarly adapted to promote the reduction of oxidized substances by the inner flame of the blow-pipe. While it enters into fusion, it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the sample under examination. But it does not co-operate in this process by its matter, nor by transposition of its constituents. If the quantity operated upon be very minute, the reduced metal will often be found in the pores of the coal. In such cases, the parts surrounding the little cavity which contained the sample are digged out with a knife, triturated in a small mortar, and the coal washed off from the metallic particles, which thereupon become visible, either in form of powder or as small and flat spangles, according to the nature of the individual metal or metals present.

In many cases, e. g. in the reduction of peroxide of tin, some borax may be advantageously added to the carbonate of soda, in order to render the mass more readily fusible. Carbonate of soda serves also as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing carbonate of soda. The sample to be examined is made into a paste with some carbonate of soda and water; and this paste is placed upon the loop of a platinum wire, and heated. A few only of the bases dissolve in melting carbonate of soda, but acids dissolve with facility therein. Silicic acid differs from all other acids, inasmuch as the glass which it forms with carbonate of soda remains clear upon cooling, provided, of course, the two constituents be present in the requisite proportions. Carbonate of soda is moreover applied as a decomposing agent and flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, whilst, at the same time, the new-formed sulphate of soda is reduced to sulphuret of sodium,—and of the sulphurets of arsenic with which it transposes to sulphuret of arsenic and sodium, and arsenite or arseniate of soda, thus converting the arsenic into a form which permits its subsequent reduction by hydrogen. Finally, carbonate of soda is the most susceptible reagent in the dry way, for the detection of manganese, since, when fused in the outer flame of the blow-pipe, in conjunction with a substance containing manganese, it produces a green, turbid button, owing to the formation of manganate of soda.

§ 81.

3. CYANIDE OF POTASSIUM. (K Cy.)

For the preparation of this reagent, vide § 42.

Uses.—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way, in fact, it excels in its action almost all other reagents of the same class, and separates the metals not only from oxygen compounds, but also from sulphur compounds; this reduction is attended, in the former case, with formation of cyanate of potash, the cyanide of potassium absorbing oxygen, and, in the latter case, with formation of sulphocyanide of potassium. By means of this reagent we may effect the reduction of metals from their compounds with the greatest possible facility; thus we may, for instance, produce pure antimony from antimonious acid or from sulphuret of antimony, metallic iron from peroxide of iron, &c., &c. The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit-lamp. Cyanide of potassium is a particularly valuable and important agent to effect the reduction of arsenites and arseniates, and more particularly of sulpharsenious acid. Compare § 95, *d.*, 10. Cyanide of potassium is equally important as a blow-pipe reagent. Its action is exceedingly energetic; substances like peroxide of tin, bisulphuret of tin, &c., the reduction of which, by means of carbonate of soda, requires a tolerably strong flame, are reduced by cyanide of potassium with the greatest facility. In blow-pipe experiments, we use invariably a mixture of equal parts of carbonate of soda and cyanide of potassium; the admixture of carbonate of soda is intended to check in some measure the excessive fusibility of the cyanide of potassium. This mixture of cyanide of potassium, with carbonate of soda, besides being a far more powerful reducing agent than the simple carbonate of soda, has moreover this great advantage over the latter, that it is imbibed by the pores of the charcoal with extreme facility, and permits thus the production of the metallic globules in a state of the greatest purity.

§ 82.

BIBORATE OF SODA. (BORAX.) ($NaO, 2BO_3$.)

The purity of commercial borax may be tested by dissolving it, and adding to the solution either carbonate of potass or solution of nitrate of barytes or of nitrate of silver; the addition of either of the two latter reagents is to be preceded by that of nitric acid. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them cause the formation of a precipitate, or render the fluid turbid, the borax will require recrystallization. The pure crystallized borax is exposed to a gentle heat, in a platinum crucible, until it ceases to swell; it is subsequently levigated when cool, and the powder is kept for use.

Uses.—Boracic acid manifests a great affinity for oxides, when brought into contact with them, in a state of fusion. This affinity enables the boracic acid, in the first place, to combine directly with oxides; 2. to expel weaker acids from their salts; and 3, to predispose metals, sulphur, &c., and haloid compounds to oxidize in the outer flame of the blow-pipe, in order to combine subsequently with the oxides. Most of the thus produced borates fuse readily, even without the aid of a flux, but far more so in conjunction with borate of soda; the latter salt acts in this operation either as a mere flux, or its action results in the formation of double salts.—Now, in the biborate of soda, we have both free boracic acid and borate of soda; the union of these two substances renders borax one of our most important blow-pipe reagents. In the process of fluxing with borax, we usually select platinum wire for a support; the loop of the wire is ignited, dipped into the borax powder, and subsequently exposed to the outer flame; a colorless button of fused borax is thus produced.

A small portion of the substance under examination is then attached to the borax button, by bringing the latter into contact with it, either whilst still hot, or having previously moistened it. The button with the sample of the substance intended for analysis thus adhering to it is now again exposed, first to the flame of a spirit-lamp, and finally to the blow-pipe flame, and the phenomena to the manifestation of which this process gives rise, are carefully observed and examined. The following points ought to be more particularly watched: 1. Whether the sample under examination dissolves tranparent or not, and whether it retains this transparency on cooling, or not; 2. whether the button exhibits a distinct and definite color; since this, in many instances, at once clearly indicates the individual metal which the analysed compound contains; such is the case, for instance, with cobalt; and 3. whether the button manifests the same or a different deportment in the outer and inner flame. Phenomena of the latter kind arise from the ensuing reduction of higher oxides to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

§ 83.

5. PHOSPHATE OF SODA AND AMMONIA. (MICROCOSMIC SALT.)

$$(P\,O_5,\ Na\,O,\ N\,H_4\,O,\ H\,O.)$$

Preparation.—Dissolve six parts of phosphate of soda and one part of pure sal ammoniac in two parts of hot water, and allow the solution to cool. Free the thus produced crystals of the double phosphate of soda and ammonia by recrystallization from the chloride of sodium which adheres to them. Dry the purified crystals, levigate them, and keep the powder for use.

Uses.—When phosphate of soda and ammonia is subjected to the action of heat, the ammonia escapes in conjunction with the water of crystallization, and a compound of similar composition to borax remains, viz., a compound which contains both a free acid and a readily fusible salt The action of microcosmic salt is therefore quite analogous to that of biborate of soda. We prefer it, however, in many cases to borax, as a solvent or flux, the buttons which it forms with many substances being more beautifully and distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop of the wire must be made small and narrow, otherwise the pearl will not stick to it. The operation is conducted as directed in the preceding paragraph.

§ 84.

PROTONITRATE OF COBALT. ($Co\,O, N\,O_5$.)

Preparation.—An intimate mixture of two parts of very finely levigated cobalt ore, four parts of nitrate of potass, one part of effloresced carbonate of soda, and one part of dry carbonate of potass, is gradually projected into a red-hot crucible; the latter is afterwards left exposed to the strongest possible heat, until the mass is in an advanced state of fusion. The fused mass is subsequently allowed to cool, and afterwards levigated, and the powder boiled with water; the impure peroxide of cobalt thus produced is thoroughly washed, and subsequently digested and heated with hydrochloric acid until dissolved. The solution, which is of a dark green color, and generally gelatinous, owing to the separation of silicic acid—is evaporated to dryness, the residue boiled with water and hydrochloric acid, filtered, and carbonate of ammonia added to the filtrate,—(which is kept boiling all the while),—until all acid reaction ceases. The filtrate is then precipitated by means of carbonate of potass; the precipitate produced is washed, and subsequently dissolved in nitric acid. The solution is evaporated to dryness, at a gentle heat, and one part of the residue dissolved in ten parts of water, for use. Since cobalt ore contains almost invariably an admixture of nickel, the solution of protonitrate of cobalt produced in this manner, is not quite free from contamination with the latter metal. This contamination, however, does not impair its fitness as a reagent.

Uses.—The protoxide of cobalt, when ignited with certain infusible substances, forms with the latter peculiarly-colored compounds, and may therefore serve for the detection of those substances. The process of ignition is conducted in the following manner. A sample of the finely-levigated substance under examination is ignited on a charcoal support, a small drop of solution of protonitrate of cobalt added, and the substance again ignited. In this process, oxide of zinc acquires an intensely green color, alumina a blue, and magnesia a faint rosy tint. The rosy tint of magnesia is of so little intensity that beginners frequently overlook this reaction. Silica likewise acquires a faint blue tint when ignited after previous moistening with solution of protonitrate of cobalt; this ought to be borne in mind when testing for alumina. The blue color of the alumina compound is, however, far more beautiful and intense than that of the silica compound.

SECTION III.

ON THE DEPORTMENT OF THE VARIOUS SUBSTANCES WITH REAGENTS.

§ 85.

I stated in my introductory remarks that the operations and experiments of qualitative analysis have for their object the conversion of the *unknown* constituents of any given compound into forms of which we *know* the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the individual constituents of which the analysed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends entirely upon the greater or less degree of certainty with which they lead to definite results, no matter whether of a positive or negative nature. But as a question does not render us a whit the wiser if we do not understand the language in which the answer is returned, so, in like manner, will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of our reagents upon the examined substance.

Before therefore we can proceed to enter upon the practical investigations of analytical chemistry, it is indispensable that we should *really* possess the most perfect knowledge of the deportment, relations, and properties of the new forms into which we intend to convert the substances which we wish to analyse. Now, this perfect knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds, and for the manifestation of the various reactions in general; and, in the second place, in a distinct impression of the color, form, and physical properties which characterize the new compound. This section of the work demands, therefore, not simply the most careful and attentive study, but requires, moreover, that the student should *examine and verify, by actual experiment, every fact asserted in it.* The method usually adopted in elementary works on chemistry is, to treat of the various substances and their behaviour with reagents individually and separately, and to point out their characteristic reactions. I have, however, in the present work, deemed it more judicious and better adapted to its elementary character, to arrange those substances which are in many respects analogous, into groups, and thus, by confronting their analogies with their differences, to place the latter in the clearest possible light.

A.—DEPORTMENT AND PROPERTIES OF THE METALLIC OXIDES.

§ 86.

First Group.

POTASS, SODA, AMMONIA.

Properties of the group.—The alkalies are readily soluble in water in their pure, or caustic state, and likewise as sulphurets and carbonates. They do not, therefore, precipitate one another, either in their pure states or as carbonates, nor are they precipitated by sulphuretted hydrogen under any condition whatever. The solutions of the pure alkalies, as well as of their sulphurets and carbonates, restore the blue color of reddened litmus paper, and impart an intensely brown tint to turmeric paper.

Special reactions.

a. POTASS. (K O.)

1. The heat of a spirit-lamp fails to volatilize potass, its hydrate and salts. Potass and its hydrate deliquesce in the air; the oily liquids which they form upon their deliquescence do not solidify by absorption of carbonic acid.

2. Nearly the whole of the salts of potass are readily soluble in water. They are colorless, provided the constituent acid be so. The neutral salts of potass with strong acids do not alter vegetable colors. Carbonate of potass crystallizes with difficulty, and deliquesces in the air. Sulphate of potass is anhydrous, and suffers no alteration in the air.

3. *Bichloride of platinum* produces in the neutral and acid solutions of the salts of potass a yellow crystalline heavy precipitate of CHLORIDE OF PLATINUM AND POTASSIUM.

$$(\mathrm{K\,Cl} + \mathrm{P\,Cl_2}.)$$

In concentrated solution, this precipitate separates immediately upon the addition of the reagent, whilst, in dilute solutions, its formation ensues only after some time. The presence of free hydrochloric acid promotes the formation of this precipitate. It is difficultly soluble in water, and wholly insoluble in alchol. Bichloride of platinum is, therefore, a particularly delicate test for salts of potass. The best method of applying this test is, to evaporate the aqueous solution of the potass salt, in conjunction with bichloride of platinum, nearly to dryness in the water-bath, and to treat the residue subsequently with alcohol, when the potassio-chloride of platinum will remain undissolved. Care must be taken not to confound this double salt with ammonio-chloride of platinum, which greatly resembles it. (Vide § 86, *c.*, 4.)

4. *Tartaric acid* produces in neutral or alkaline solutions of potass salts — (in the latter case the reagent is to be added until the fluid acquires a strongly acid reaction) — a white, quickly subsiding, *granular* crystalline precipitate of BITARTRATE OF POTASS.

$$(KO, \bar{T} + HO, \bar{T}).$$

In concentrated solutions, this precipitate separates immediately; in dilute solutions, frequently only after the lapse of some time. Violent agitation of the fluid promotes its formation considerably. Free alkalies and free mineral acids dissolve the precipitate; it is difficultly soluble in cold, but readily soluble in hot water. Acid solutions must first be neutralized with pure soda or carbonate of soda, before they can be tested for potass with tartaric acid.

5. When salts of potass are held, by means of a platinum wire, in the apex of the inner *blow-pipe flame*, the outer flame acquires a VIOLET tint; this arises from reduction of the potass and subsequent re-oxidation of the reduced potassium. The tint which phosphate and borate of potass imparts to the outer blow-pipe flame is scarcely perceptible. Presence of soda obscures this reaction completely.

6. When a salt of potass is heated with a small quantity of

water, alcohol added, and the latter ignited, the flame appears VIOLET. The presence of soda obscures this reaction likewise.

b. SODA. ($Na\,O$.)

1. Soda, its hydrate, and salts, present in general the same deportment and properties as potass and its corresponding compounds. The oily fluid which soda forms upon its deliquescence in the air re-solidifies speedily by absorption of carbonic acid. Carbonate of soda crystallizes readily; the crystals effloresce rapidly when exposed to the air. The same applies to sulphate of soda.

2. *Antimoniate of potass* produces in neutral or alkaline solutions of salts of soda a white crystalline precipitate of ANTIMONIATE OF SODA.

$$(Na\,O,\ Sb\,O_5.)$$

In concentrated solutions, this precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Violent agitation of the mixture promotes the separation of the precipitate. If the fluid, after the addition of the reagent, be stirred with a glass rod, moving the latter along the sides of the glass containing the fluid, the lines described by the rod will, even in very dilute solutions, become visible, since the precipitate commences to form at those parts that have been touched by the rod. The presence of salts of potass with neutral reaction does not interfere with the formation of the precipitate. Carbonate of potass, however, prevents its separation wholly or partially, according to the greater or less proportion in which it is present. In cases, therefore, where the solution under examination contains carbonate of potass, it is necessary to precede the application of the antimoniate of potass by the addition of hydrochloric or acetic acid until the reaction of the solution remains only feebly alkaline. Acid solutions require first to be neutralized with potass, since otherwise the reagent would suffer decomposition, and hydrated antimonic acid or biantimoniate of potass be precipitated from it.

3. Salts of soda, when exposed in a platinum wire to the inner *blow-pipe flame,* color the outer flame INTENSELY YELLOW, owing to reduction of the soda and subsequent reoxidation of the reduced sodium. This reaction remains clearly perceptible, although the soda contain a considerable admixture of potass.

4. When a salt of soda is heated with a small quantity of water, *alcohol* added, and the latter ignited, the flame appears strongly YELLOW. The presence of a salt of potass does not impair the distinctness of this reaction.

5. *Bichloride of platinum* produces no precipitate in solutions of salts of soda : *tartaric acid* only when they are highly concentrated. The BITARTRATE OF SODA, which, in such cases, crystallizes out after the lapse of some time, appears invariably in the shape of small needles and columns, and not, like the corresponding salt of potass, in the form of a granular crystalline precipitate.

c. AMMONIA. (NH_3.)

1. Pure ammonia is gaseous at the common temperature ; but we have most frequently to deal with it in its aqueous solution, in which it may be at once detected by its penetrating odor. It is expelled from its aqueous solution by the application of heat.

2. All the salts of ammonia are volatile at a high temperature, either with or without decomposition. Most of them are readily soluble in water. These solutions are colorless. The neutral compounds of ammonia with strong acids do not alter vegetable colors.

3. When salts of ammonia are triturated with *hydrate of lime,*—(but with the addition of a few drops of water,)—or are, either in solid form or in solution, heated with potass ley, the ammonia is liberated in its gaseous state, and manifests itself, 1, by its characteristic *odor ;* 2, by its *reaction* on moistened test-papers ; and 3, by giving rise to the formation of *white fumes,* when any object (e. g. a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought into con-

tact with it. These fumes arise from the formation of solid ammoniacal salts. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of mistake.

4. *Bichloride of platinum* manifests the same deportment with salts of ammonia as with salts of potass; the yellow precipitate of CHLORIDE OF PLATINUM AND AMMONIUM ($NH_4Cl + PtCl_2$) is, however, of a somewhat lighter color than potassio-chloride of platinum.

5. *Tartaric acid* produces in solutions of salts of ammonia a precipitate of BITARTRATE OF AMMONIA, ($NH_4O, \overline{T} + HO, \overline{T}$.) This precipitate is formed in the same manner, and under the same circumstances, as the corresponding salt of potass, but is somewhat more readily soluble than the latter.

Recapitulation and remarks.—The salts of potass and soda are not volatile at a common red heat, whilst the salts of ammonia volatilize readily; the latter may therefore be easily separated from the former by ignition.—The expulsion of ammonia from its compounds, by potass or lime, affords the surest means of detecting the presence of this substance. Salts of potass can be detected *positively*, only after the removal of the ammoniacal salts which may be present, since both these substances manifest the same or a similar deportment with bichloride of platinum and tartaric acid.—After the removal of the ammonia, the potass is clearly and positively characterized by either of these two reagents. The most simple way of detecting the potass in the potassio-chloride of platinum and bitartrate of potass, is to decompose these salts by ignition. The ignited potassio-chloride of platinum yields the potass in the form of chloride of potassium; the ignited bitartrate yields it in the form of carbonate of potass. With respect to soda, antimoniate of potass has now been added to the hitherto exceedingly limited means of positive detection of this substance, (such as the form of the crystals, and the general deportment and properties of some of its salts, and the yellow tint which its salts impart to the blow-pipe flame and to the flame of alcohol.) This reagent, however, effects the desired object only when applied with a careful and attentive consideration of the attendant circumstances. The most indispensable condition of its applicability is, that besides soda or potass, no other bases be present in the solution, since the salts of the heavy metallic oxides, those of the earths and alkaline earths, and finally those of ammonia, are likewise precipitated by antimoniate of potass.

§ 87.

SECOND GROUP.

BARYTES—STRONTIA—LIME—MAGNESIA.

Properties of the group.—The alkaline earths are soluble in water in their pure (caustic) state, and as sulphurets. (Magnesia, however, dissolves but very sparingly in water.) These solutions manifest alkaline reaction; magnesia manifests its alkaline reaction most clearly when placed upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water.—The solutions of the salts of the alkaline earths are, consequently, precipitated by alkaline carbonates and phosphates, whilst sulphuretted hydrogen fails to precipitate them under any condition. This deportment distinguishes the oxides of the second group from those of the first. The alkaline earths and their salts are non-volatile and colorless.

Special Reactions.

a. BARYTES. (Ba O.)

1. Caustic barytes is pretty readily soluble in hot water, but rather difficultly soluble in cold water; it dissolves readily in dilute hydrochloric or nitric acid. Hydrate of barytes does not lose its water, upon ignition.

2. Most of the salts of barytes are insoluble in water. The soluble salts do not affect vegetable colors, and are decomposed upon ignition, with the exception of chloride of barium. The

insoluble salts dissolve in hydrochloric acid, with the exception of sulphate of barytes.—Nitrate of barytes and chloride of barium are insoluble in alcohol, and do not deliquesce in the air.

3. *Ammonia* produces no precipitate in the solutions of salts of barytes; *potass* (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of CRYSTALS OF BARYTES ($Ba\,O, H\,O + 9$ aq.) produced by potass.

4. *Alkaline carbonates* throw down from solutions of barytes CARBONATE OF BARYTES, ($Ba\,O, C\,O_2$,) in the form of a white precipitate. In acid solutions, however, complete precipitation takes place only upon heating the fluid; the same is the case when carbonate of ammonia is used as the precipitant. The presence of salts of ammonia does not interfere with the formation of the precipitate.

5. *Sulphuric acid*, and all the soluble *sulphates*, produce, even in the most highly dilute solutions of barytes, immediately, a fine white precipitate of SULPHATE OF BARYTES, ($Ba\,O, S\,O_3$,) which is insoluble in acids and alkalies.

6. *Hydrofluo-silicic acid* throws down from solutions of barytes SILICOFLUORIDE OF BARIUM, ($Ba\,Fl + Si\,Fl_2$,) in the form of a colorless, crystalline, quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is nearly insoluble in hydrochloric and nitric acid.

7. *Phosphate of soda* produces in neutral or alkaline solutions of barytes, a white precipitate of PHOSPHATE OF BARYTES, ($P\,O_5$, $2\,Ba\,O, H\,O$,) which is soluble in free acids. Addition of ammonia does not increase the quantity of this precipitate, nor does it promote its formation.

8. *Oxalic acid* produces only in concentrated solutions of barytes a white precipitate of OXALATE OF BARYTES, ($Ba\,O, \overline{O}$,) which is soluble in acids. Addition of ammonia renders this reaction far more susceptible, and it is only in highly dilute solutions that the joint action of oxalic acid and ammonia fails to produce a precipitate.

9. Salts of barytes, when heated with diluted *spirit of wine*,

impart to the flame of the latter a YELLOWISH color, not, however, very characteristic.

b. STRONTIA. ($Sr O$.)

1. Strontia and its hydrate, and salts, manifest nearly the same general deportment and properties as barytes and its corresponding compounds.—Hydrate of strontia is more difficultly soluble in water than hydrate of barytes.—Chloride of strontium dissolves in absolute alcohol, nitrate of strontia is soluble in dilute alcohol; neither of the two latter compounds deliquesce in the air.

2. The salts of strontia manifest with *ammonia* and *potass,* as well as with the *alkaline carbonates* and with *phosphate of soda,* the same deportment as the salts of barytes.

3. *Sulphuric acid* and *sulphates* precipitate from solutions of strontia, SULPHATE OF STRONTIA, ($Sr O, S O_3$,) in the form of a white powder, which is insoluble in acids and alkalies. Sulphate of strontia is far more soluble in water than sulphate of barytes; owing to this solubility, the precipitated sulphate of strontia separates from rather dilute solutions in general only after the lapse of some time; and this is invariably the case (even in concentrated solutions) if *solution of gypsum* is used as the precipitant.

4. *Hydrofluo-silicic acid* fails to produce any precipitate, even in concentrated solutions of strontia.

5. *Oxalic acid* precipitates even from tolerably dilute solutions; after the lapse of some time, OXALATE OF STRONTIA, ($Sr O, \bar{O}$,) in the form of a white powder. Addition of ammonia promotes the formation of the precipitate greatly, and increases its quantity considerably.

6. If salts of strontia, which are soluble in water or alcohol, be heated with dilute alcohol, and the latter be subsequently ignited, the flame will appear of an intense CARMINE RED color, more particularly upon stirring the alcoholic mixture. This color must not be confounded with that which salts of lime impart to the flame of alcohol.

c. LIME. ($Ca\,O$.)

1. Lime and its hydrate and salts present, in their general deportment and properties, a great similarity with barytes and strontia and their corresponding compounds. Hydrate of lime is far more difficultly soluble in water than the hydrates of barytes and strontia; it dissolves, moreover, more sparingly in hot than in cold water. Hydrate of lime loses its water upon ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol, and deliquescent in the air.

2. *Ammonia, potass, alkaline carbonates,* and *phosphate of soda,* present the same deportment with salts of lime as with salts of barytes.

3. *Sulphuric acid* and *sulphate of soda* produce immediately in highly-concentrated solutions of lime white precipitates of SULPHATE OF LIME, ($Ca\,O$, $S\,O_3$,) which redissolve completely in a large amount of water, and are far more soluble still in acids. In less concentrated solutions the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in highly dilute solutions. Solution of gypsum, of course, cannot produce a precipitate in solutions of lime; but even a cold saturated solution of sulphate of potash, mixed with an equal amount of water, fail to produce a precipitate in these solutions, at least immediately. In solutions of lime, which are so highly dilute that sulphuric acid fails to precipitate them, a precipitate will immediately form upon the addition of alcohol, in conjunction with the sulphuric acid.

4. *Hydrofluo-silicic acid* does not precipitate salts of lime.

5. *Oxalic acid* produces a white precipitate of OXALATE OF LIME, ($Ca\,O$, $\overline{O}$,) even in highly dilute neutral solutions of lime. Addition of ammonia promotes the formation of this precipitate, and increases its quantity. Oxalate of lime is readily soluble in hydrochloric acid and nitric acid, but not perceptibly so in acetic acid, nor in oxalic acid.

6. Soluble salts of lime, when heated with dilute *alcohol,*

impart to the flame of the latter a YELLOWISH RED color, which is often confounded with that communicated to the flame of alcohol by salts of strontia.

d. MAGNESIA. ($Mg\,O$.)

1. Magnesia and its hydrate are white powders of far greater bulk than barytes, strontia and lime, and their hydrates. Magnesia and hydrate of magnesia are nearly insoluble both in cold and hot water. Hydrate of magnesia loses its water upon ignition.

2. Some of the salts of magnesia are soluble in water, the rest are insoluble. The soluble salts of magnesia have a nauseous, bitter taste; they do not alter vegetable colors, when in a neutral state; with the exception of sulphate of magnesia, they undergo decomposition, when ignited, and the greater part of them even upon simple evaporation of their solutions. All the salts of magnesia which are insoluble in water, dissolve readily in hydrochloric acid.

3. *Ammonia* throws down from the solutions of neutral salts of magnesia, a part of the magnesia as HYDRATE, ($Mg\,O, H\,O$,) in the form of a white bulky precipitate. The rest of the magnesia remains in solution as a double salt, viz. in combination with the ammoniacal salt which forms upon the decomposition of the salts of magnesia; these double salts of ammonia and magnesia are not decomposable by ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds, that ammonia fails to precipitate salts of magnesia in presence of ammoniacal salts, or, what comes to the same point, that ammonia produces no precipitate in acid solutions of magnesia; and that precipitates produced by ammonia in neutral solutions of magnesia, are re-dissolved upon the addition of an ammoniacal salt.

4. *Potass* and *caustic barytes* precipitate from solutions of magnesia, HYDRATE OF MAGNESIA. The separation of this precipitate is greatly promoted by boiling the mixture. Salts of am-

monia re-dissolve the precipitated hydrate of magnesia, and prevent its precipitation altogether when added in sufficient quantity to the magnesia solution, previously to the addition of the precipitant. If the solution be subsequently boiled, however, with an excess of potass, the precipitate will of course make its appearance, since this process causes the decomposition of the ammoniacal salt and subsequent expulsion of the ammonia, removing thus the agent which retained the hydrate of magnesia in solution.

5. *Carbonate of potass* produces in neutral solutions of magnesia a white precipitate of BASIC CARBONATE OF MAGNESIA.

$$3\,(Mg\,O,\,C\,O_2+aq)+Mg\,O,\,H\,O.$$

One fourth of the carbonic acid of the carbonate of potass is liberated upon the decomposition of this salt, and combines with a portion of the new-formed carbonate of magnesia to bicarbonate which remains in solution. This carbonic acid escapes upon ebullition; the application of heat will therefore promote the separation, and increase the quantity of the precipitate. Salts of ammonia prevent this precipitation, and redissolve precipitates already formed.

6. *Carbonate of ammonia* fails to precipitate solutions of magnesia in the cold, and precipitates them but imperfectly upon ebullition. The presence of salts of ammonia prevents the formation of a precipitate altogether.

7. *Phosphate of soda* precipitates from not *too* highly dilute solutions of magnesia, PHOSPHATE OF MAGNESIA,

$$(P\,O_5,\,2\,Mg\,O,\,H\,O)$$

as a white powder. The separation of the precipitate is greatly promoted by ebullition. But if ammonia be added to the solution of magnesia, no matter whether before or after the addition of the phosphate of soda, a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA

$$(P\,O_5,\,2\,Mg\,O,\,N\,H_4\,O)$$

will separate, even though the solution be highly dilute, in the latter case the separation may be greatly promoted and accelerated by vigorous stirring with a glass rod; even should the solution be so extremely dilute as to forbid the formation of a precipitate; yet the lines of direction, in which the glass rod has moved along the sides of the vessel, will after the lapse of some time appear distinctly as white streaks. Chloride of ammonium and salts of ammonia in general, fail to dissolve the basic phosphate of magnesia and ammonia, but this double salt is soluble in free acids, even in acetic acid.

8. *Oxalate of ammonia* (but not free oxalic acid) produces a white precipitate of OXALATE OF MAGNESIA.

$$(\mathrm{Mg\,O}, \bar{\mathrm{O}}.)$$

Salts of ammonia prevent its formation.

9. *Sulphuric acid* and *hydrofluosilicic acid* fail to precipitate salts of magnesia.

10. If magnesia, or a salt of magnesia, be moistened with solution of *protonitrate of cobalt,* and subsequently exposed upon a charcoal support to the continued action of a strong *blow-pipe flame,* a mass will be produced of a faint flesh tint, which becomes distinct only upon cooling, but is never very intense.

Recapitulation and remarks.—The difficult solubility of the hydrate of magnesia, the ready solubility of the sulphate of magnesia, and the disposition of salts of magnesia to form double salts with ammoniacal compounds, are the three principal points in which magnesia differs from the other alkaline earths. We select for the positive detection of magnesia invariably the reaction with phosphate of soda, applied in conjunction with ammonia. Should barytes, strontia, or lime be present, these earths are to be removed first, before proceeding to apply the special test for magnesia; this removal may be effected either by heating the fluid under examination with carbonate of ammonia in conjunction with sal ammoniac, or by heating it with sulphate of potass and oxalate of ammonia in conjunction with sal ammoniac. The detection of barytes is an easy task under any circumstances, since the precipitate of sulphate of barytes which separates from barytes solutions immediately upon the addition of solution of gypsum, and the reaction of barytes with hydrofluosilicic acid are indubitable proofs of the presence of this earth. Strontia may likewise readily be detected by its deportment with solution of gypsum, provided, of course, no barytes be present. Should barytes be present, this substance is to be removed first before proceeding to test for the strontia. The separation of strontia from barytes is best effected by converting both earths into dry chlorides, and subsequently digesting the latter with absolute alcohol, when the chloride of strontium will dissolve, whilst the chloride of barium will remain undissolved. When testing for strontia by means of the alcohol flame, the operator must take care not to confound the color which strontia imparts to this flame with that communicated to it by salts of lime. — For the positive detection of lime, we invariably select oxalic acid first. Before applying this test, however, barytes and strontia are to be removed, since the deportment which these substances manifest with oxalic acid is analogous to that presented by lime, differing from it simply in intensity. The removal of barytes and strontia is effected by means of sulphate of potash ; it may happen in this process that a portion of the lime precipitates in conjunction with the barytes and strontia. This is, however, a matter of indifference, since there remains always a sufficient amount of lime in solution to permit the positive and indubitable detection of this substance by oxalic acid. The best way of effecting the detection of the alkaline earths in this phosphate is to decompose the latter by means of perchloride of iron in conjunction with acetate of potass, (vide § 99, *a.*, 8). The oxalates of the alkaline earths are converted into carbonates by ignition preparatory to the detection of the individual earths which they contain. Sulphate of barytes and sulphate of strontia are fluxed with alkaline carbonates, for the purpose of detecting the barytes and strontia. Compare § 98, 5.

§ 88.

Third Group.

ALUMINA. OXIDE OF CHROMIUM.

Properties of the group.—Alumina and oxide of chromium are insoluble in water, both in their pure state and as hydrates. They form no neutral salts with carbonic acid. Their sulphurets cannot be produced in the humid way. Sulphuretted hydrogen, consequently, fails to precipitate solutions of alumina and of oxide of chromium; hydrosulphuret of ammonia precipitates the hydrated oxides from these solutions. This deportment with hydrosulphuret of ammonia distinguishes the oxides of the third, from those of the two preceding groups.

Special Reactions.

a. ALUMINA. ($Al_2 O_3$.)

1. Alumina is non-volatile and colorless; the hydrate of alumina is also colorless. Alumina dissolves in acids slowly and with very great difficulty. Hydrate of alumina in an amorphous state is readily soluble in acids; but its crystals dissolve with very great difficulty in these menstrua. After previous ignition, in conjunction with alkalies, alumina is readily dissolved by acids.

2. The salts of alumina are colorless, and most of them are non-volatile; some of them are soluble, others insoluble. The soluble salts have a sweetish astringent taste, redden litmus paper, and lose their acids, upon ignition. The insoluble salts are dissolved by hydrochloric acid, with the exception of some natural compounds of alumina, which latter may be rendered soluble in acids, by ignition in conjunction with carbonate of soda.

3. *Potass* throws down from the solutions of alumina a bulky precipitate of HYDRATE OF ALUMINA,

$$(Al_2 O_3 3 H O,)$$

which contains an admixture of potass, and generally also of basic salt, and redissolves readily and completely in an excess of the precipitant, from which solution it will precipitate again upon addition of chloride of ammonium, even in the cold; but more completely still upon heating the solution, (compare § 23.) The presence of salts of ammonia does not prevent this precipitation by potass.

4. *Ammonia* also produces in solutions of alumina a precipitate of HYDRATE OF ALUMINA, containing an admixture of ammonia and of basic salt; and this precipitate is likewise redissolved by a very considerable excess of the precipitant; this re-solution, however, ensues only with more or less considerable difficulty, according to the greater or less amount of ammoniacal salts which the solution of alumina may happen to contain in admixture.

It is this deportment of ammonia and ammoniacal salts with alumina, which accounts for the complete precipitation of hydrate of alumina from potass solution by an excess of chloride of ammonium.

5. If alumina, or a compound of alumina, be ignited upon charcoal, before the blow-pipe, and subsequently moistened with a few drops of solution of *protonitrate of cobalt*, and then again strongly ignited, an unfused mass will be produced of a deep SKY-BLUE color, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candle-light it appears violet.

b. OXIDE OF CHROMIUM. ($Cr_2\ O_3$.)

1. Oxide of chromium is a green, its hydrate a bluish-grey-green powder. Oxide of chromium occurs in two modifications, of which the one is dissolved slowly by dilute acids, whilst the other is altogether insoluble in dilute acids, and dissolves but very slowly even in boiling concentrated sulphuric acid. The application of an intense heat causes the conversion of the soluble into the insoluble modification; this transmutation is attended with vivid incandescence. Hydrated oxide of chromium is readily soluble in acids.

2. The two modifications of the oxide of chromium are found in its salts. The salts corresponding to the insoluble modification are of a bright violet color, and insoluble in water

and acids; whilst those corresponding to the soluble modification are green, partly soluble and partly insoluble in water, but, without exception, soluble in hydrochloric acid.—Many of the green salts are converted into the insoluble modification by the action of heat; this transmutation being attended with a change of color from green to violet; by fluxing in conjunction with carbonate of soda, these salts are re-converted into the soluble modification.—The solutions of the salts of oxide of chromium exhibit a highly characteristic, blackish green color, even though highly dilute. The solution of some of the double salts of oxide of chromium, such as sulphate of chromium and alumina, oxalate of chromium and potass, &c. &c., appear of a blackish violet color.—The soluble salts of oxide of chromium redden litmus;—those with volatile acids are decomposed upon ignition.

3. *Potass* produces in solutions of oxide of chromium a bluish-green precipitate of HYDRATED OXIDE OF CHROMIUM, ($Cr_2 O_3$. 5 H O,) which dissolves readily and completely in an excess of the precipitant, imparting an emerald-green tint to the fluid. Upon *long-continued* ebullition of the fluid, the whole of the hydrated oxide will again separate, and the supernatant fluid will accordingly appear perfectly colorless. The same reprecipitation will take place if chloride of ammonium be added to the potass solution, and the mixture subsequently heated.

4. *Ammonia* produces in solutions of oxide of chromium the same precipitate of HYDRATED OXIDE OF CHROMIUM as potass; a small portion of these precipitates redissolves in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red tint; but if, after the addition of the excess of ammonia, heat be applied to the mixture, the whole of the hydrated oxide of chromium will precipitate.

5. The fusion of oxide of chromium or of any of its compounds with a *mixture of nitrate of potass and carbonate of soda*, invariably gives rise to the formation of an ALKALINE CHROMATE, part of the oxygen of the nitric acid separating from the nitrate of potass, and converting the oxide of chromium into chromic acid,

which combines subsequently with the potass of the decomposed nitre and with the soda of the carbonate. For the deportment and properties of chromic acid, vide § 97. *b.*

6. *Phosphate of soda and ammonia* dissolves oxide of chromium and its salts both in the *oxidizing* and *reducing* flame of the blow-pipe, into clear buttons of a faint YELLOW-GREEN tint which, upon cooling, changes to EMERALD-GREEN. The oxide of chromium and its salts manifest a similar deportment with *borax.*

Recapitulation and remarks.—The solubility of the hydrates of alumina and oxide of chromium in potass, and their re-precipitation from these potass solutions by chloride of ammonium, enable us to effect, in the first place, the separation of alumina and oxide of chromium from the oxides of other groups, and, in the second place, the *individual* and *positive* detection of alumina, when oxide of chromium is absent. Should the latter substance be present—(which will either appear at once from the color of the solution, or may be readily ascertained, at all events, from the deportment of the substance under examination when exposed to the blow-pipe flame in conjunction with microcosmic salt,)—it must first be removed before the operator can proceed to test for alumina. The separation of oxide of chromium from alumina may be effected completely, by fusing the mixed oxides, in conjunction with nitre. The precipitation of oxide of chromium, which ensues upon long-continued ebullition of the solution of the oxide in potass, is generally sufficiently complete and accurate, but in some cases gives rise to mistakes. It is, moreover, finally to be borne in mind, that alkalies produce no precipitates in the solutions of alumina and oxide of chromium, when non-volatile organic substances are present, such as sugar, tartaric acid, &c., &c.

§ 89.

Fourth Group.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—PEROXIDE OF IRON.

Properties of the group.—The sulphurets corresponding with the oxides of the fourth group are more or less soluble in dilute acids, but insoluble in water, alkalies, and alkaline sulphurets. Sulphuretted hydrogen fails, therefore, altogether to produce a precipitate in solutions of the salts of these oxides when these solutions contain free acid ; neutral solutions are either not at all or but imperfectly precipitated by this reagent ; but alkaline solutions are completely precipitated by sulphuretted hydrogen. From neutral solutions of the salts of the oxides of this group the corresponding sulphurets will precipitate if an alkaline sulphuret be substituted for sulphuretted hydrogen.

Special Reactions.

a. OXIDE OF ZINC. (ZnO.)

1. The oxide of zinc and its hydrate are white powders, which dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid. The oxide of zinc acquires a lemon-yellow tint when heated, but it reassumes its original white color upon cooling.

2. The compounds of oxide of zinc are colorless. Its soluble neutral salts redden litmus paper, and are readily decomposed by heat, with the exception of sulphate of zinc, which can bear a faint red heat, without undergoing decomposition.

3. *Sulphuretted hydrogen* precipitates from neutral solutions of salts of zinc a portion of this metal as white SULPHURET OF ZINC (ZnS.) In acid solutions, this reagent fails altogether to produce a precipitate, if the free acid present is one of the stronger acids.

4. *Hydrosulphuret of ammonia* throws down from *neutral* as *sulphuretted hydrogen* does from *alkaline* solutions of salts

of zinc, the whole of the metal as SULPHURET OF ZINC, in the form of a white precipitate. This precipitate is not redissolved by an excess of hydrosulphuret of ammonia, nor by potass or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid.

5. *Potass and ammonia* throw down from solutions of salts of zinc, HYDRATED OXIDE OF ZINC ($Zn\,O, H\,O$) in the form of a white gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant.

6. *Carbonate of potass* produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC

$$(3\,[Zn\,O,\ H\,O] + 2\,[Zn\,O,\ C\,O_2])$$

which is insoluble in an excess of the precipitant. The presence of salts of ammonia prevents the formation of this precipitate, and the addition of such salts causes the re-solution of precipitates already formed, owing to the ammoniacal salts combining with the oxide of zinc to soluble double salts of oxide of zinc and ammonia.

7. *Carbonate of ammonia* also produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC, but this precipitate redissolves upon further addition of the precipitant.

8. When a mixture of oxide of zinc, or of one its salts with *carbonate of soda* is exposed to the *reducing flame* of the blow-pipe, the charcoal support becomes covered with a slight incrustation of OXIDE OF ZINC, which presents a yellow color while hot, and turns white upon cooling. This incrustation is caused by the reduced metallic zinc volatilizing at the moment of its reduction, and reoxidizing in passing through the outer flame.

9. If oxide of zinc, or one of the salts of zinc, be moistened with solution of *protonitrate of cobalt*, and subsequently heated before the blow-pipe, an unfused mass will be obtained, of a beautiful GREEN color; this mass is a compound of oxide of zinc with protoxide of cobalt.

b. PROTOXIDE OF MANGANESE. ($Mn\,O$.)

1. Protoxide of manganese exhibits a grey-greenish color; the hydrated protoxide is white. Both the protoxide and its hydrate are peroxidized, and turn brown, when exposed to the air. They are readily soluble in hydrochloric acid, nitric acid, and sulphuric acid.

2. The protosalts of manganese are colorless or of a pale red color; some of them are soluble, others insoluble. The soluble salts, with the exception of protosulphate, are readily decomposed by a red-heat. The solutions of the soluble protosalts of manganese do not alter vegetable colors.

3. *Sulphuretted hydrogen* fails to precipitate acid solutions of protosalts of manganese; neutral solutions, this reagent precipitates *but very imperfectly*.

4. *Hydrosulphuret of ammonia* throws down from neutral, as sulphuretted hydrogen does from alkaline, solutions of the protosalts of manganese, the whole of this metal as SULPHURET OF MANGANESE ($Mn\,S$) in the form of a bright flesh-colored precipitate, which turns dark-brown upon exposure to the air; this precipitate is insoluble in hydrosulphuret of ammonia and in alkalies, but readily soluble in hydrochloric acid and nitric acid.

5. *Potass* and *ammonia* produce whitish precipitates of HYDRATED PROTOXIDE OF MANGANESE ($Mn\,O$, $H\,O$), which, upon exposure to the air, speedily acquire a brownish, and, finally, a deep blackish-brown color, owing to the ensuing conversion of the hydrated protoxide into hydrated peroxide, by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate, but the presence of sal ammoniac prevents the precipitation by ammonia altogether, and that by potass partly. Solution of sal ammoniac redissolves only those parts of *already formed* precipitates which have not yet undergone peroxidation. The solution of the hydrated protoxide of manganese in sal ammoniac is entirely owing to the disposition of the protosalts of manganese to form double salts

with salts of ammonia. Pellucid solutions of double salts of manganese and ammonia turns brown, when exposed to the air, and deposit dark-brown hydrated peroxide of manganese.

$$(Mn_2 O_3, 2 HO)$$

6. If any of the compounds of manganese be fused in conjunction with *carbonate of soda,* in the *outer* flame of the blowpipe, upon a platinum wire, MANGANATE OF SODA

$$(Na O, Mn O_3)$$

will be formed, which will make the fused mass appear GREEN while hot, and of a BLUE-GREEN tint after cooling, the button at the same time becoming turbid. This reaction enables us to detect the smallest quantities of manganese. The delicacy of the test may be still further increased by the addition of a minute quantity of nitre to the carbonate of soda.

7. *Borax* and *phosphate of soda and ammonia* dissolve manganese compounds, in the *outer* flame of the blow-pipe, into clear VIOLET-RED buttons, which, upon cooling, acquire an AMETHYST-RED tint; these buttons lose their color in the *inner* flame, owing to an ensuing reduction of the peroxide to protoxide. The button which borax forms with manganese, appears black when containing a considerable proportion of peroxide of manganese, but the button formed by phosphate of soda and ammonia never loses its transparency. The latter loses its color, in the inner flame of the blow-pipe, far more readily than the former.

c. PROTOXIDE OF NICKEL. ($Ni O.$)

1. Protoxide of nickel is a grey, its hydrate a green powder. Both the protoxide and its hydrate are unalterable in the air, and readily soluble in hydrochloric acid, nitric acid, and sulphuric acid.

2. The protosalts of nickel are in their anhydrous state, for the most part yellow, and in their hydrated state, green; their solutions are of a light green color. The soluble neutral salts redden litmus paper, and are decomposed at a red-heat.

3. *Sulphuretted hydrogen* fails to precipitate solutions of salts

of nickel containing free mineral acid; in neutral solutions this reagent precipitates *them but very imperfectly.*

4. *Hydrosulphuret of ammonia* produces in neutral, as sulphuretted hydrogen does in alkaline, solutions of protosalts of nickel, a black precipitate of SULPHURET OF NICKEL, (Ni S,) which is not altogether insoluble in hydrosulphuret of ammonia, containing an admixture of free ammonia or of pentasulphuret of ammonium; it is owing to this slight solubility of the sulphuret of nickel in sulphuret of ammonium, that the fluid from which it has been thrown down exhibits, in most cases, a brownish color. Sulphuret of nickel dissolves with great difficulty in hydrochloric acid, but readily in aqua regia.

5. *Potass* produces a light green precipitate of HYDRATED PROTOXIDE OF NICKEL, (Ni O, H O,) which is insoluble in potass, and unalterable in the air. Carbonate of ammonia redissolves this precipitate to a greenish-blue fluid, from which potass re-precipitates the nickel, as a yellow-green hydrated protoxide of nickel.

6. *Ammonia* likewise produces a precipitate of HYDRATED PROTOXIDE OF NICKEL; but this redissolves readily in an excess of the precipitant as a double salt of protoxide of nickel and ammonia, the solution exhibiting a blue color. Potass reprecipitates hydrated protoxide of nickel from this solution. Ammonia fails to produce a precipitate in solutions of protosalts of nickel which contain ammoniacal salts or free acid.

7. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL, (Ni Cy,) which redissolves readily in an excess of the precipitant as a double cyanide of nickel and potassium, (Ni Cy + K Cy). The solution exhibits a brownish yellow color. Upon adding sulphuric acid or hydrochloric acid to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel re-precipitated; the latter substance is very difficultly soluble in an excess of the precipitant acid, in the cold, but readily so, upon boiling.

8. *Borax* and *phosphate of soda and ammonia* dissolve com-

pounds of protoxide of nickel, in the *outer* flame of the blowpipe, to clear buttons of a dark yellow color, with a shade of red-brown; upon cooling, these buttons grow lighter, and finally almost colorless. Addition of nitre or carbonate of potass changes the color to blue or to a dark purple. The button which phosphate of soda and ammonia forms with protosalts of nickel, remains unaltered in the *inner* flame of the blow pipe, but that of borax turns grey and turbid from reduced metallic nickel.

d. PROTOXIDE OF COBALT. (Co O.)

1. Protoxide of cobalt is a grey, its hydrate a pale red powder. Both the protoxide and its hydrate dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid.

2. The protosalts of cobalt are blue in their anhydrous, and of a characteristic bright red tint in their hydrated state. Their solutions show this color even though considerably diluted. The soluble neutral salts redden litmus paper, and are decomposed at a red heat

3. *Sulphuretted hydrogen* fails to precipitate acid solutions of cobalt, and precipitates neutral solutions at the most, but very incompletely, when they contain weak acids; the precipitates are of a black color.

4. *Hydrosulphuret of ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions of protosalts of cobalt, the whole of this metal as black SULPHURET OF COBALT. (Co S) This substance is insoluble in alkalies and hydrosulphuret of ammonia, difficultly soluble in hydrochloric acid, but readily soluble in aqua regia.

5. *Potass* produces in solutions of cobalt BLUE precipitates of basic salts of cobalt, which turn GREEN upon exposure to the air, owing to the absorption of oxygen, and are, upon boiling, converted into the pale red hydrated protoxide of cobalt, which appears generally rather discolored from an admixture of peroxide which is formed in the process. These precipitates are insoluble in potass; but neutral carbonate of ammonia dissolves them com-

pletely to intensely violet-red fluids, in which potass produces none, or, *at the most,* but a *very scanty,* precipitate.

6. *Ammonia* produces the same precipitate as potass, but this redissolves in an excess of the ammonia to a reddish-brown fluid, in which potass produces none, or, *at the most,* but a *very scanty,* precipitate. Ammonia fails to precipitate solutions of protosalts of cobalt containing ammoniacal salts or free acids.

7. The addition of *cyanide of potassium* to a solution of cobalt acidified with some hydrochloric acid, gives rise to the formation of a brownish white precipitate of PROTOCYANIDE OF COBALT, ($Co\ Cy$,) which dissolves readily as a double cyanide of cobalt and potassium, ($Cy_6\ Co_2 + 3\ K = 2\ C\ Ky + 3\ K$,) when heated with an excess of the precipitant, in presence of free hydrocyanic acid. Acids cause no precipitation in the solutions of this double salt.

8. *Borax* dissolves compounds of cobalt both in the *inner* and *outer* flame of the blow-pipe, into clear buttons of a magnificent BLUE color, which verges almost upon black, when the cobalt is present in considerable proportion. This test is as delicate as it is characteristic. *Phosphate of soda and ammonia* manifests with salts of cobalt, before the blow-pipe, an analogous but less intense reaction.

e. PROTOXIDE OF IRON. ($Fe\ O$.)

1. Protoxide of iron is a black powder; hydrated protoxide of iron is a white powder, which in a moist state absorbs oxygen, and turns speedily grey green, and finally brown red; both the protoxide and its hydrate are readily soluble in hydrochloric acid, sulphuric acid, and nitric acid.

2. The protosalts of iron have a greenish color; their solutions appear colored only when quite concentrated. When exposed to the air, they absorb oxygen, and become converted into salts of the ferroso-ferric oxide. The soluble neutral salts redden litmus paper, and are decomposed at a red heat.

3. Acid solutions are not precipitated by *sulphuretted hydrogen,*

neutral solutions, with weak acids, *but incompletely*; the precipitates are of a black color.

4. *Hydrosulphuret of ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions of protosalts of iron, the whole of this metal as black SULPHURET OF IRON, ($Fe\,S$,) which is insoluble in alkalies and alkaline sulphurets, but readily soluble in hydrochloric acid and nitric acid.

5. *Potass* and *ammonia* produce a precipitate of HYDRATED PROTOXIDE OF IRON, ($Fe\,O, H\,O$,) which, in the first moment, looks almost white, but acquires, after a very short time, a dirty green, and finally a reddish-brown color, owing to absorption of oxygen from the air. The presence of salts of ammonia prevents the precipitation by potass partly, and that by ammonia altogether. If the alkaline solution of protoxide of iron, which is thus obtained by the agency of ammoniacal salts, be subsequently exposed to the air, hydrated peroxide of iron will precipitate.

6. *Ferrocyanide of potassium* produces in solutions of protoxide of iron a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON, ($2\,Cfy + K + 3\,Fe$,) which, by absorption of oxygen from the air, speedily acquires a blue color, the whole of the potassium, and one equivalent of iron of every three equivalents of the compound being oxidized, so as to leave two equivalents of Prussian blue ($3\,Cfy + 2\,Fe_2$) behind. Nitric acid or chlorine effect this oxidation immediately.

7. *Ferricyanide of potassium* produces a magnificently blue-colored precipitate of FERRICYANIDE OF IRON, ($2\,Cfy + 3\,Fe$.) This precipitate does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potass. In highly dilute solutions of protosalts of iron, this ferricyanide of potassium produces simply a deep blue-green coloration.

8. *Sulphocyanide of potassium* does not alter solutions of protoxide of iron, free from admixture of peroxide.

9. *Borax* dissolves protosalts of iron in the *oxidizing* flame, into DARK RED BUTTONS, the color of which changes to bottle green in

the *inner* flame, owing to the ensuing reduction of the new-formed peroxide to magnetic-oxide. Both tints disappear totally, or in a great measure, upon the refrigeration of the buttons. *Phosphate of soda and ammonia* manifest a similar deportment with the protosalts of iron; the buttons produced by the latter reagent lose their color, upon cooling, more completely still than in the case with the buttons produced by borax.

f. PEROXIDE OF IRON. ($Fe_2\ O_3$.)

1. Peroxide of iron is a more or less deep-colored red-brown powder; hydrated peroxide of iron has a somewhat lighter color. Both the protoxide and its hydrate dissolve in hydrochloric acid, nitric acid, and sulphuric acid; the hydrate dissolves readily in these acids, but the oxide dissolves with greater difficulty, especially after ignition.

2. The persalts of iron are of a more or less reddish yellow color. Their solutions exhibit this color even though highly diluted. The soluble neutral salts redden litmus paper, and are decomposed by heat.

3. *Sulphuretted hydrogen,* when added to a neutral or acid solution of a persalt of iron, decomposes with the latter; the hydrogen reduces the persalt of iron to the state of a protosalt, by withdrawing from the peroxide of iron one-third of its oxygen, with which it forms water; part of the sulphur of the decomposed sulphuretted hydrogen separates in a highly-divided state, and imparts a TURBID and MILKY appearance to the fluid.

4. *Hydrosulphuret* of *ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions of persalt of iron, the whole of this metal as black SULPHURET OF IRON, (Fe S.) This precipitation is preceded by the reduction of the persalt to a protosalt. In very dilute solutions, the reagent produces only a blackish-green coloration. The minutely divided protosulphuret of iron subsides in such cases only after long standing. Sulphuret of iron, as already stated, (*e.* 4.), is insoluble in alkalies and alkaline sulphurets, but readily soluble in hydrochloric acid and nitric acid.

5. *Potass* and *ammonia* produce bulky reddish-brown precipitates of HYDRATED PEROXIDE OF IRON, ($Fe_2 O_3, H O$,) which are insoluble in an excess of the precipitant as well as in salts of ammonia.

6. *Ferrocyanide of potassium* produces, even in highly dilute solutions, a magnificently blue precipitate of SESQUIFERROCYANIDE OF IRON, ($3 Cfy + 2 Fe_2$,) (Prussian blue,) which is insoluble in hydrochloric acid, but is readily decomposed by potass, with precipitation of peroxide of iron.

7. *Ferricyanide of potassium* deepens the color of solutions of persalts of iron to a ruddy brown, but it fails to produce a precipitate.

8. *Sulphocyanide of potassium* imparts to neutral or acid solutions of persalts of iron a most intense blood-red color, arising from the formation of a soluble SULPHOCYANIDE OF IRON. This test is the most delicate of all; it will indicate the presence of peroxide of iron even in fluids which are so highly dilute that every other reagent fails to produce the slightest visible alteration. The red coloration may, in such cases, be detected most distinctly, by resting the test-tube upon a sheet of white paper, and looking into it at the top.

9. The persalts of iron present the same deportment and phenomena as the protosalts, when exposed to the action of the *blowpipe flame,* vide *c.* 9. (protoxide of iron.)

Recapitulation and remarks.—Of the metallic oxides belonging to the fourth group, oxide of zinc alone is soluble in potass. It is this property which distinguishes oxide of zinc from the other oxides of this group, and connects it with those of the third group. But it differs from alumina and oxide of chromium, inasmuch as it is re-precipitated from solution in potass, by sulphuretted hydrogen. This property of the oxide of zinc to dissolve in potass, and to precipitate from this solution upon the addition of sulphuretted hydrogen, affords a safe and positive means of detecting the presence of this oxide. The protoxides of manganese, nickel, cobalt, and iron, form with ammoniacal compounds, soluble double salts, from which free ammonia fails to precipitate the metallic oxides: but peroxide of iron, like the oxides of the third group, is completely precipitated by ammonia, even though salts of ammonia be present. Hence it follows, in the first place, that this property of the protoxides enumerated will serve to effect the separation of manganese, nickel, and cobalt, both from peroxide of iron and from alumina and oxide of chromium;—and, in the second place, that, in order to separate these metals from protoxide of iron, the latter substance must first be peroxidized, which is best effected by boiling its solution with nitric acid. Peroxide of iron differs from alumina and oxide of chromium, inasmuch as it is insoluble in potass; and the peroxide of iron may be distinguished from the protoxide, by means of ferrocyanide of potassium.—The hydrated protoxides of nickel and cobalt dissolve in carbonate of ammonia, whilst hydrated protoxide of manganese is insoluble in this substance. We may, therefore, by means of this solvent, separate the protoxide of manganese from the two other oxides. The brown tint which the white hydrated protoxide of manganese assumes when exposed to the air, and the blow-pipe reactions, and more particularly that with carbonate of soda, are the most positive tests for protoxide of manganese.—Cyanide of nickel and cyanide of cobalt are both soluble in cyanide of potassium. But cyanide of nickel is re-precipitated from this solution by acids, which is not the case with cyanide of cobalt, if the solution contained free acid, and has been heated. The formation of a precipitate upon the addition of hydrochloric acid to a solution of these two cyanides in cyanide of potassium, proves the presence of nickel most positively under any circumstances. Whether this precipitate be cyanide of nickel or cobalticyanide of nickel, is quite immaterial as far as the *detection of nickel* is concerned: all we have to bear in mind is simply this, that no precipitate will form if cobalt alone be present in the solution, since cobalticyanide of potassium is not decomposed by hydrochloric acid. In order to get at the composition of the various precipitates which are formed by hydrochloric acid in solution of the mixed cyanides of nickel and cobalt, and to comprehend the general process of their formation, we have to assume and consider three special and distinct cases, differing from one another in the relative proportions of nickel and cobalt, which the solutions under examination respectively contain.

1, Ni : Co : : 3 eq. : 2 eq.
2, Ni : Co : : 3 eq. : 2 eq. + x
3, Ni : Co : : 3 eq. + x : 2 eq.

The solution will, in the first case, contain one eq. of cobalticyanide of potassium, ($Cy_6\ Co_2 + 3\ K$,) and 3 eq. of double cyanide of nickel and potassium, ($Cy_3\ Ni_3 + Cy_3\ K_3$); now, upon the addition of hydrochloric acid in excess to this solution, the double cyanide of nickel and potassium suffers decomposition, and the potassium of the cobalticyanide of potassium transposes with the nickel of the cyanide of nickel; the products of this process of double decomposition and transposition are chloride of potassium, hydrocyanic acid, and cobalticyanide of nickel, ($Cy_6\ Co_2 + 3\ Ni$,) which latter separates in the form of a dirty green precipitate, containing the *whole* of the nickel and cobalt present in the solution.—In the second case we obtain equally a precipitate of cobalticyanide of nickel, but this precipitate, though containing the whole of the *nickel*, does *not* contain *all* the *cobalt* of the solution, since the excess of cobalticyanide of potassium is not decomposed.—In the third case, we obtain a precipitate of cobalticyanide of nickel, which contains the *whole* of the *cobalt* and a *portion* of the *nickel*, mixed with insoluble cyanide of nickel which contains the rest of the nickel. The cobalticyanide of nickel has been formed here in the same manner as in the first case, whilst the cyanide of nickel owes its formation to the decomposition of the *excess* of the double cyanide of nickel and potassium. Hence it is evident, that the presence of nickel is invariably indispensable to the formation of a precipitate, and consequently, that the production of a precipitate is the most positive proof of the presence of this metal. Since cobalt is always, and under any circumstances, to be readily and positively detected by its characteristic deportment before the blow-pipe, any further remarks respecting the mere *detection* of either metal would be superfluous. But as we are already so far advanced towards effecting the complete separation of nickel from cobalt, it may be as well here to touch briefly upon this point.—In the first and second of the above-mentioned cases, we need simply, after the addition of the hydrochloric acid, expose the fluid, with the therein suspended precipitate of cobalticyanide of nickel to the action of heat, until the free hydrocyanic acid is expelled,—(this operation leaves both the cobalticyanide of nickel and the excess of cobalticyanide of potassium which remains undecomposed in the second case, unaltered)—and subsequently add caustic potass, with which the cobalticyanide of nickel will at once decompose and transpose to cobalticyanide of potassium, which remains in solution, and protoxide of nickel which precipitates in the hydrated state.—But in the third case, it is necessary to add a larger quantity of hydrochloric acid, and to boil the mixture subsequently, until the cyanide of nickel contained in the precipitate, and which would only be imperfectly decomposed by potass, is converted into chloride of nickel, and until the hydrocyanic acid, which is disengaged during this process, is completely expelled; the mixture is then to be boiled with caustic potass, when the whole of the nickel will separate as insoluble hydrated protoxide, whilst the whole of the cobalt will remain in solution as cobalticyanide of potassium. It is necessary finally to mention, that alkalies fail to precipitate the oxides of the fourth group in presence of non-volatile organic substances, (such as sugar, tartaric acid, &c.) We have already seen that the same applies to alumina and oxide of chromium.

§ 90.

Fifth Group.

OXIDE OF SILVER—PROTOXIDE OF MERCURY—PEROXIDE OF MERCURY—OXIDE OF LEAD—OXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

Properties of the group.—The sulphurets corresponding with the oxides of this group, are insoluble both in dilute acids and in alkaline sulphurets. The solutions of these oxides are therefore completely precipitated by sulphuretted hydrogen, no matter whether their reaction be neutral, alkaline, or acid.

For the sake of greater clearness and simplicity, we divide the oxides of this group into two sections, and distinguish

1. OXIDES PRECIPITABLE BY HYDROCHLORIC ACID, viz.: oxide of silver, protoxide of mercury, oxide of lead.

2. OXIDES, NOT PRECIPITABLE BY HYDROCHLORIC ACID, viz.: peroxide of mercury, oxide of copper, oxide of bismuth, oxide of cadmium.

Lead must be considered in both sections, since the difficult solubility of its chloride may lead to confounding its oxide with protoxide of mercury and oxide of silver, without affording us, on the other hand, any means of effecting its perfect separation from the oxides of the second section.

§ 91.

FIRST SECTION OF THE FIFTH GROUP: OXIDES PRECIPITABLE BY HYDROCHLORIC ACID.

Special Reactions.

a. OXIDE OF SILVER. (Ag O.)

1. Oxide of silver is a grey brown powder which dissolves readily in dilute nitric acid. It forms no hydrate.

2. The salts of oxide of silver are non-volatile and colorless; most of them acquire a black tint when exposed to the light. The

soluble neutral salts do not alter vegetable colors, and are decomposed at a red heat.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* precipitate black SULPHURET OF SILVER, (Ag S,) which is insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. Boiling concentrated nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

4. *Potass* and *ammonia* precipitate from solutions of salts of silver, the oxide of this metal in the form of a LIGHT BROWN POWDER, which is insoluble in potass, but dissolves readily in ammonia. The presence of salts of ammonia prevents this precipitation totally or partly.

5. *Hydrochloric acid* and *soluble metallic chlorides* produce in solutions of salts of silver a white curdy precipitate of CHLORIDE OF SILVER. (Ag Cl.) In very dilute solutions, these reagents impart simply a bluish-white opalescent appearance to the fluid. Chloride of silver, when exposed to the light, acquires first a violet tint, and then turns black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound the chloride of silver is separated again by acids. Chloride of silver, when heated, fuses without decomposition, into a transparent horny mass.

6. When compounds of silver, mixed with *carbonate of soda*, are exposed on a charcoal support to the *inner* flame of the blowpipe, WHITE BRILLIANT AND DUCTILE METALLIC GLOBULES are produced unattended with any incrustation of the charcoal.

b. PROTOXIDE OF MERCURY. (Hg_2 O)

1. Protoxide of mercury is a black powder which is readily soluble in nitric acid, and is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

2. The salts of protoxide of mercury, when ignited, volatilize either unaltered, or they are decomposed, and the mercury vola-

tilizes in the metallic state. Most of the protosalts of mercury are colorless. The soluble salts redden litmus paper in the neutral state; when mixed with much water, they decompose into insoluble basic and soluble acid salts.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce black precipitates of PROTOSULPHURET OF MERCURY. (Hg_2 S,) which are insoluble, both in dilute acids, in hydrosulphuret of ammonia, and cyanide of potassium. Sulphuret of potassium resolves this sulphuret into bisulphuret, which dissolves, and globules of metallic mercury, which separate. Protosulphuret of mercury is readily decomposed and dissolved by aqua regia, but not by boiling concentrated nitric acid.

4. *Potass* and *ammonia* produce in the solution of protosalts of mercury black precipitates, which are insoluble in an excess of the precipitants. The potass precipitates consist of PROTOXIDE OF MERCURY; whilst those produced by ammonia consist of a BASIC DOUBLE SALT OF PROTOXIDE OF MERCURY AND AMMONIA, e. g.

$$(N H_3, N O_5 + 3 Hg_2 O.)$$

5. *Hydrochloric acid* and *soluble metallic chlorides* precipitate PROTOCHLORIDE OF MERCURY (Hg_2 Cl) as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves, however, although very difficultly and slowly, upon long protracted boiling with these acids, being resolved by hydrochloric acid into perchloride of mercury and metallic mercury, which separates, and converted by nitric acid into perchloride of mercury and pernitrate of mercury. Aqua regia and chlorine water dissolves the protochloride of mercury readily as perchloride. Ammonia and potass decompose the protochloride of mercury and separate black protoxide from it.

6. If a drop of a neutral or feebly acid solution of protoxide of mercury be poured on a *clean and smooth surface of copper*, and washed off after some time, the spot will subsequently when rubbed with cloth, paper, &c., appear WHITE and LUSTROUS like

silver. The application of heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and removes the silvering.

7. *Protochloride of tin* produces in solutions of protoxide of mercury, a grey precipitate of METALLIC MERCURY, which may be united into globules by heating and agitation, but most readily by boiling with hydrochloric acid.

8. If an intimate mixture of any of the compounds of mercury, with anhydrous *carbonate of soda* be introduced into a drawn-out glass tube, and covered with a layer of carbonate of soda, and the tube be then heated before the blow-pipe, the mercurial compound will undergo decomposition, and metallic mercury will separate, forming a crust of grey sublimate above the heated part of the tube. The minute particles of mercury may be united into globules by rubbing this crust with a glass rod.

c. OXIDE OF LEAD. ($Pb\,O$.)

1. Oxide of lead is a yellow or reddish-yellow powder which fuses to a vitreous mass when heated. Hydrated oxide of lead is white. Both the oxide of lead and its hydrate dissolves in nitric acid and acetic acid.

2. The salts of oxide of lead are colorless and non-volatile; the soluble salts, in the neutral state, redden litmus paper, and are decomposed at a red heat.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce black precipitates of SULPHURET OF LEAD, ($Pb\,S$,) which are insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. Sulphuret of lead is decomposed by boiling concentrated nitric acid; the whole of the lead is converted, at first, into nitrate of lead, and the greater portion of the sulphur separates, whilst another portion is converted into sulphuric acid. The sulphuric acid thus formed decomposes a portion of the nitrate of lead, and forms sulphate of lead, which remains undissolved in the form of a white powder, mixed with the separated sulphur.—In solutions of salts of lead containing an excess of

a mineral acid, sulphuretted hydrogen produces a precipitate only after the addition of water.

4. *Potass* and *ammonia* throw down BASIC SALTS OF LEAD in the form of white precipitates, which are insoluble in ammonia, and of difficult solution in potass. Ammonia fails to produce a precipitate in solutions of acetate of lead, owing to the formation of a soluble tri-acetate of lead.

5. *Carbonate of potass* throws down from solutions of salts of the oxide of lead, a white precipitate of CARBONATE OF LEAD ($Pb O, C O_2$,) which is insoluble in an excess of the precipitant and also in cyanide of potassium.

6. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions of salts of the oxide of lead heavy white precipitates of CHLORIDE OF LEAD, ($Pb Cl$,) which are soluble in a large amount of water, especially upon the application of heat. This chloride of lead is not altered by ammonia, and is more difficult of solution in dilute hydrochloric and nitric acid than in water.

7. *Sulphuric acid* and *sulphates* produce white precipitates of SULPHATE OF LEAD, ($Pb O, SO_3$,) which are nearly insoluble in water and dilute acids. From dilute solutions, and especially from solutions which contain much free acid, the sulphate of lead precipitates only after some time, and frequently even after the lapse of a considerable time. It is advisable, under all circumstances, to add a tolerably large *excess* of dilute sulphuric acid, since sulphate of lead is far more insoluble in dilute sulphuric acid than in water. Sulphate of lead is slightly soluble in concentrated nitric acid; it dissolves, with difficulty, in boiling concentrated hydrochloric acid, but more readily in potass ley.

8. *Chromate of potass* produces a yellow precipitate of CHROMATE OF LEAD, ($Pb O, Cr O_3$,) which is readily soluble in potash, but insoluble in dilute nitric acid.

9. When a mixture of any of the compounds of lead with *carbonate of soda,* is exposed on a charcoal support, to the *reducing flame of the blow-pipe,* soft and ductile METALLIC GLOBULES

OF LEAD are readily produced, the charcoal becoming covered, at the same time, with a slight yellow incrustation of OXIDE OF LEAD.

Recapitulation and remarks.—The metallic oxides of the first section of the fifth group are the most distinctly characterized in their corresponding chlorides, since the different deportment of these chlorides with ammonia affords us a simple means both of detecting and of separating them from one another. For the chloride of silver, as I have stated, is dissolved by ammonia, whilst protochloride of mercury and chloride of lead remain undissolved. From the solution of ammonio-chloride of silver which is obtained by treating chloride of silver with ammonia, the simple chloride of silver may be re-precipitated by nitric acid; this reaction admits of no mistake and we require, accordingly, no other means to effect the positive detection of silver. Of the two remaining chlorides, the protochloride of mercury is converted by ammonia into black protoxide of mercury, whilst the chloride of lead remains unaltered. The newly-formed protoxide of mercury may be separated from the chloride of lead by treating the mixed chlorides with nitric acid, which dissolves the protoxide of mercury, or by boiling with water, which effects the solution of the chloride of lead. The protoxide of mercury is sufficiently characterized by the deportment of the corresponding chloride with ammonia. Sulphuric acid and chromate of potass are the most positive tests for the oxide of lead.

§ 92.[1]

SECOND SECTION OF THE FIFTH GROUP. OXIDES WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

a. PEROXIDE OF MERCURY. (Hg O.)

1. Peroxide of mercury forms a crystalline mass of a light red color, inclining sometimes to orange, which upon levigation yields a powder of a yellowish red color. When heated

it transitorily acquires a deeper tint; at a faint red heat, it is resolved into metallic mercury and oxygen. The hydrate of peroxide of mercury is yellow. Both the peroxide of mercury and its hydrate dissolve readily in hydrochloric acid and nitric acid.

2. The salts of peroxide of mercury volatilize upon ignition; part of them suffer decomposition in this process, whilst others remain unaltered. Most of the persalts of mercury are colorless. The soluble salts in their neutral state redden litmus paper. The nitrate and sulphate of peroxide of mercury are decomposed into soluble acid and insoluble basic salts, when treated with a larger amount of water.

3. When a very small amount of *sulphuretted hydrogen* or of *hydrosulphuret of ammonia* is added to solutions of persalts of mercury, and the mixture is subsequently agitated, a perfectly white precipitate is produced. The addition of somewhat large quantities of these reagents causes the precipitate to acquire a yellow, orange, or brown-red color, according to the less or greater proportion added; an excess of the reagent produces a purely black precipitate of PERSULPHURET OF MERCURY, ($Hg\,S$.) This progressive variation of color from white to black, which depends on the gradually increasing proportions of the sulphuretted hydrogen, or hydrosulphuret of ammonia distinguishes the peroxide of mercury from all other substances. The white precipitate which forms at first, consists of a double compound of persulphuret of mercury with the still undecomposed portion of the persalt of mercury, (e. g. in a solution of perchloride of mercury, $Hg\,Cl + 2\,Hg\,S$;) the gradually increasing admixture of black persulphuret causes the precipitate subsequently to pass through the various gradations of color which I have mentioned. Persulphuret of mercury is not dissolved by hydrosulphuret of ammonia, nor by potass or cyanide of potassium; it is altogether insoluble in hydrochloric acid and nitric acid, even upon boiling. It dissolves completely in sulphuret of potassium and is readily decomposed and dissolved by aqua regia.

4. *Potass*, when added in a small proportion to neutral or

feebly acid solutions of peroxide of mercury, produces a reddish brown precipitate, which acquires a yellow tint when the reagent is added in excess. The *reddish brown* precipitate is a BASIC SALT; the *yellow*, on the contrary, consists of HYDRATED PEROXIDE OF MERCURY. ($Hg\,O, 3\,H\,O$.) An excess of the precipitant does not re-dissolve these precipitates. In very acid solutions this reaction either does not take place at all, or is at least but incomplete. In presence of salts of ammonia, potass produces in solutions of persalts of mercury, *white* precipitates, consisting of double compounds of the divers persalts of mercury with amide of mercury. Thus, for instance, from a solution of perchloride of mercury containing ammoniacal salts in admixture, potass throws down a double compound of perchloride of mercury with amide of mercury, ($Hg\,Cl + Hg\,N\,H_2$.)

5. *Ammonia* produces in solutions of persalts of mercury the same WHITE PRECIPITATE, which potass produces when salts of ammonia are present.

6. *Protochloride of tin*, when added in small portions to salts of peroxide of mercury, reduces the peroxide to protoxide, giving thus rise to the subsequent formation of a white precipitate of PROTOCHLORIDE OF MERCURY, ($Hg_2\,Cl$;) but when added in excess, this reagent deprives the mercury of the whole of its oxygen and acid or of the whole of the salt-radical, and accordingly throws the mercury down in the metallic state, just as is the case with protoxide of mercury, (vide § 91, *b.* 7.) The precipitate, therefore, which in the first place was white, acquires now a grey tint, and may be readily united into globules of metallic mercury, by boiling with hydrochloric acid.

7. The persalts of mercury present the same deportment with metallic *copper* as the protosalts; and the same applies to their deportment when heated, in admixture with *carbonate of soda*, in a glass tube before the blow-pipe.

b. OXIDE OF COPPER. ($Cu\,O$.)

1. Oxide of copper is black, fixed powder; its hydrate is of a

light blue color. Both the oxide of copper and its hydrate dissolve readily in hydrochloric acid, sulphuric acid, and nitric acid.

2. Most of the neutral salts of oxide of copper are soluble in water; the soluble salts redden litmus, and suffer decomposition, when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are white in the anhydrous state; the hydrated salts are of blue or green color, which their solutions continue to exhibit, even though much diluted.

3. *Sulphuretted hydrogen* and *hydrosulphuret* of ammonia produce, in alkaline, neutral, and acid solutions of salts of copper, blackish brown precipitates of PERSULPHURET OF COPPER ($Cu\,S$.) This sulphuret is insoluble in dilute acids and caustic alkalies, and equally so in hot solutions of sulphuret of potassium and of sulphuret of sodium; but it is not altogether insoluble in hydrosulphuret of ammonia; the latter reagent is, therefore, not adapted to effect the perfect separation of persulphuret of copper from other metallic sulphurets. Persulphuret of copper is readily decomposed and dissolved by boiling concentrated nitric acid; it dissolves, likewise, completely in solution of cyanide of potassium. In solutions of salts of copper which contain an excess of concentrated mineral acid, sulphuretted hydrogen produces a precipitate only after the addition of water.

4. *Potass* produces a light blue, bulky precipitate of HYDRATED OXIDE OF COPPER, ($Cu\,O, HO$) If the solution be highly concentrated, and the potass be added in excess, the precipitate will, after the lapse of some time, turn black, and lose its bulkiness, even in the cold; but, at all events, upon boiling with the fluid in which it is suspended, and which, if necessary, is to be diluted for this purpose. In this process the hydrated oxide is converted into simple oxide.

5. *Carbonate of potass* produces, in solutions of salts of copper, a greenish-blue precipitate of HYDRATED BASIC CARBONATE OF COPPER,

$$(Cu\,O, CO_2 + Cu\,O, HO,)$$

which, upon boiling, changes to brown blackish oxide of copper, and dissolves in ammonia to an azure blue, and in cyanide of potassium, to a brownish fluid.

6. *Ammonia*, when added in a small portion to solutions of salts of copper, produces a GREENISH BLUE precipitate, consisting of a BASIC SALT OF COPPER. This precipitate redissolves readily in an excess of the precipitant, yielding a perfectly clear solution of a magnificent azure blue, which owes its color to the formation of a BASIC DOUBLE SALT OF AMMONIO-OXIDE OF COPPER. Thus, for instance, in a solution of sulphate of copper ammonia produces a precipitate of

$$(N\,H_3, Cu\,O + N\,H_4\,O, S\,O_3).$$

The blue coloration of the fluid ceases to be perceptible only upon diluting the solution considerably. Potass produces in such blue solutions in the cold, after the lapse of some time, a precipitate of blue hydrated oxide of copper, but, upon boiling, this reagent precipitates the whole of the copper as black oxide. Carbonate of ammonia presents the same deportment with salts of copper, as pure ammonia.

7. *Ferrocyanide of potassium* produces even in highly dilute solutions, a ruddy-brown precipitate of FERROCYANIDE OF COPPER ($Cfy + 2\ Cu$) which is insoluble in dilute acids, but suffers decomposition when acted upon by potass.

8. *Metallic iron*, when brought into contact with concentrated solutions of salts of copper, is almost immediately covered with a COPPERY-RED CRUST OF METALLIC COPPER; highly dilute solutions produce this coating only after the lapse of some time. This test is extremely delicate; the reaction becomes most speedily manifest when the solution contains a free acid, (hydrochloric acid.)

9. When a mixture of any of the compounds of copper with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blow-pipe*, METALLIC COPPER is obtained without simultaneous incrustation of the charcoal. The best

method of freeing this copper from the surrounding particles of charcoal, is to triturate the whole mass in a small mortar with some water, and to wash the charcoal powder subsequently off. The coppery-red metallic spangles will remain.

c. OXIDE OF BISMUTH. ($Bi\ O_3$.)

1. Oxide of bismuth is a yellow powder which transitorily acquires a deeper tint when heated; it fuses at a red-heat. Hydrated oxide of bismuth is white. Both the oxide of bismuth and its hydrate dissolve readily in hydrochloric acid, sulphuric acid, and nitric acid.

2. The salts of bismuth are non-volatile, with the exception of a few, (chloride of bismuth.) Most of them are decomposed at a red-heat. They are colorless; some of them are soluble in water, whilst others are insoluble in this menstruum. The soluble salts, in the neutral state, redden litmus paper, and are decomposed into soluble acid and insoluble basic salts when treated with a large amount of water.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce, in neutral and acid solutions of salts of bismuth, black precipitates of SULPHURET OF BISMUTH ($Bi\ S_3$) which are insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium, but are readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of bismuth which contain an excess of concentrated hydrochloric or nitric acid, sulphuretted hyrogen produces a precipitate only after the addition of water.

4. *Potass* and *ammonia* throw down from solutions of salts of bismuth, HYDRATED OXIDE OF BISMUTH as a white precipitate, which is insoluble in an excess of the precipitants.

5. *Carbonate of potass* throws down from solutions of salts of bismuth, BASIC CARBONATE OF BISMUTH ($Bi\ O_3,\ CO_2$) as a white bulky precipitate, which is insoluble in an excess of the precipitant, and equally so in cyanide of potassium.

6. *Chromate of potass* precipitates from solutions of salts of

bismuth CHROMATE OF BISMUTH as a yellow powder. This substance differs from chromate of lead, inasmuch as it is soluble in dilute nitric acid, and insoluble in potass.

7. The reaction which characterizes the oxide of bismuth, more particularly, is the decomposition of its neutral salts by *water* into acid soluble and basic insoluble salts. The addition of a large amount of water to solutions of salts of bismuth causes the immediate formation of a dazzling white precipitate, provided there be not a too considerable proportion of free acid present. This reaction is the most susceptible in the case of chloride of bismuth, since the basic chloride of bismuth ($Bi\ Cl_3,\ 2\ Bi\ O_3$) is nearly absolutely insoluble in water. Should water fail to produce a precipitate in nitric solutions of bismuth, owing to the presence of a too considerable portion of free acid, a precipitate will immediately form, upon neutralizing the free acid with an excess of basic acetate of lead; we must, of course, be fully convinced of the absence of sulphuric acid, &c., before we can have recourse to the application of this means. From the basic salts of antimony which are formed under analogous circumstances, the precipitated basic salts of bismuth may be readily distinguished by their insolubility in tartaric acid.

8. When a mixture of any of the compounds of bismuth, with *carbonate of soda,* is exposed on a charcoal support, to the *reducing flame of the blow-pipe,* BRITTLE GRAINS OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered, at the same time, with a slight yellow incrustation of OXIDE OF BISMUTH.

d. OXIDE OF CADMIUM. ($Cd\ O$.)

1. Oxide of cadmium is a yellowish brown, fixed powder. The hydrated oxide is white. Both the oxide of cadmium and its hydrate dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid.

2. The salts of oxide of cadmium are either colorless or white;

most of them are soluble in water. The soluble salts, in the neutral state, redden litmus paper, and are decomposed at a red-heat.

3. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce, in alkaline, neutral, and acid solutions of salts of cadmium, a bright yellow precipitate of SULPHURET OF CADMIUM, ($Cd\,S$), which is insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium, but is readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of cadmium which contain a considerable excess of free acid, sulphuretted hydrogen produces a precipitate only after the addition of water.

4. *Potass* produces, in solutions of salts of cadmium, a white precipitate of HYDRATED OXIDE OF CADMIUM ($Cd\,O, H\,O$) which is insoluble in an excess of the precipitant.

5. *Ammonia* likewise precipitates from solutions of salts of cadmium white HYDRATED OXIDE OF CADMIUM, but this redissolves readily to a colorless fluid, upon addition of ammonia in excess.

6. *Carbonate of potass* and *carbonate of ammonia* produce white precipitates of CARBONATE OF CADMIUM ($Cd\,O, C\,O_2$) which are insoluble in an excess of the precipitants. The presence of salts of ammonia does not prevent the formation of these precipitates. The precipitated carbonate of cadmium dissolves readily in solution of cyanide of potassium.

7. When a mixture of any of the compounds of cadmium with *carbonate of soda* is exposed on a charcoal support, to the *reducing flame of the blow-pipe*, the charcoal becomes covered with a reddish yellow incrustation of OXIDE OF CADMIUM, owing to the volatilization of the reduced metal and its subsequent reoxidation in passing through the oxidizing flame.

Recapitulation and remarks.—The perfect separation of the metallic oxides of the second section of the fifth group, from protoxide of mercury and oxide of silver, may, as I have already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from oxide of lead. The peroxide of mercury differs from the other oxides of this section, inasmuch as the corresponding sulphuret is insoluble in boiling nitric acid. This property affords a convenient means for its separation. Moreover, the reactions with protoxide of tin, or with metallic copper, as well as those in the dry way, will readily indicate the presence of peroxide of mercury, after the previous removal of the protoxide.

Of the remaining oxides, those of copper and cadmium differ from those of lead and bismuth, inasmuch as the precipitates which ammonia causes in solutions of the salts of the former, are soluble in an excess of ammonia, whilst the precipitates which this reagent produces in solutions of the salts of the latter do not redissolve in an excess of the precipitant. The oxide of bismuth may be separated from the oxide of lead by means of sulphuric acid; but the most characteristic reaction of the oxide of bismuth is, as I have already stated, the decomposition of its salts by water. For the surest tests for lead, I refer to § 91, *c.*, 7 and 8. The oxide of copper may be separated from the oxide of cadmium, by means of carbonate of ammonia; the former is more particularly characterized by the reactions with ferrocyanide of potassium and with iron, and likewise by the deportment of its salts before the blow-pipe, whilst the oxide of cadmium may invariably be detected by its yellow sulphuret, which is insoluble in hydrosulphuret of ammonia, and by the characteristic incrustation with which its salt covers the charcoal support when exposed to the reducing flame of the blow-pipe. For the method of separating the oxides of the fifth group from one another by means of cyanide of potassium, I refer to the second section of Part II. (Additional remarks to § 120.)

§ 93.

Sixth Group.

PEROXIDE OF GOLD—PEROXIDE OF PLATINUM—OXIDE OF ANTIMONY—PEROXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS AND ARSENIC ACID *

Properties of the group.—The sulphurets corresponding with the oxides of the sixth group are insoluble in dilute acids. They combine with alkaline sulphurets, forming soluble sulphur salts, in which they perform the part of the acid. Sulphuretted hydrogen, consequently precipitates these oxides completely from acidified, but not from alkaline solutions. The precipitated sulphurets dissolve in hydrosulphuret of ammonia, sulphuret of potassium, &c. and re-precipitate from these solutions upon the addition of acids.

We divide the oxides of this group into two classes, and distinguish,

1. OXIDES, OF WHICH THE CORRESPONDING SULPHURETS ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, viz. peroxide of gold and peroxide of platinum.

2. OXIDES, OF WHICH THE CORRESPONDING SULPHURETS ARE SOLUBLE IN HYDROCHLORIC ACID OR NITRIC ACID, viz. oxide of antimony, protoxide and peroxide of tin, arsenious and arsenic acid.

§ 94.

First Class.

Special Reactions.

a. PEROXIDE OF GOLD. ($Au\ O_3$.)

1. Peroxide of gold is a black brown powder; its hydrate is

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* I have placed the two acids of arsenic with the metallic oxides, since the deportment of sulphuret of arsenic may readily lead to confounding them with some of the oxides of the sixth group, and because in the systematic course of analysis the sulphuret of arsenic is invariably precipitated in conjunction with sulphuret of antimony, sulphuret of tin, &c. &c.

chestnut brown. Both the peroxide of gold and its hydrate are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric acid and sulphuric acid dissolve the peroxide of gold; water re-precipitates it from these solutions.

2. Salts of gold with oxygen acids are at present nearly altogether unknown. The haloid salts of gold are yellow, and their solutions continue to exhibit this tint up to a high degree of dilution. The whole of them are readily decomposed upon ignition; the soluble salts, in the neutral state, redden litmus paper.

3. *Sulphuretted hydrogen* precipitates from neutral and acid solutions of salts of gold, the whole of the metal as black PERSULPHURET OF GOLD ($Au\ S_3$) which is insoluble in simple acids, partly soluble in potass, and perfectly so in sulphuretted alkaline sulphurets and in aqua regia.

4. *Hydrosulphuret of ammonia* produces the same precipitate, which redissolves in an excess of the precipitant only if the latter contains an excess of sulphur in admixture.

5. *Potass* produces in tolerably concentrated solutions of salts of gold a reddish yellow precipitate of PEROXIDE OF GOLD, which acquires a deeper tint upon boiling, is insoluble in an excess of potass, and contains invariably salts, or chloride of gold, and potass in admixture. Potass fails to precipitate acid solutions of salts of gold in the cold.

6. *Ammonia* produces likewise only in tolerably concentrated solutions of salts of gold, reddish yellow precipitates of AURATE OF AMMONIA (fulminating gold). In solutions which contain free acid or ammoniacal salts, this precipitate forms only upon boiling.

7. *Protochloride of tin*, containing an admixture of perchloride, produces even in extremely dilute solutions of gold, a purple-red precipitate, (or coloration at least,) which sometimes inclines rather to violet or to brown-red. This precipitate, which has received the name of PURPLE OF CASSIUS, is insoluble in hydrochloric acid. May not this substance be considered as a compound of peroxide of tin with metallic gold?

8. *Protosalts of iron* reduce the peroxide of gold when added to its solutions, and precipitate metallic gold in the form of a very fine brown powder, which acquires metallic lustre, when pressed upon with the blade of a knife, or when rubbed. The fluid in which the precipitate is suspended, appears of a blackish-blue color, by transmitted light.

b. PEROXIDE OF PLATINUM. ($Pt\,O_2$.)

1. Peroxide of platinum is a blackish-brown, its hydrate a redish brown powder. Both the peroxide of platinum and its hydrate are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids.

2. The persalts of platinum are decomposed at a red heat. They are of a reddish-brown color, which their solutions continue to exhibit even though considerably diluted. The soluble salts in the neutral state redden litmus paper.

3. *Sulphuretted hydrogen* throws down from acid and neutral solutions—(but not from alkaline solutions, at all events, not completely)—after the lapse of some time a blackish-brown precipitate of BISULPHURET OF PLATINUM ($Pt\,S_2$). This precipitate forms *immediately* when the solution is heated, after the addition of the sulphuretted hydrogen. It is soluble in a considerable excess of potass or of alkaline sulphurets, and more particularly of those of the higher class. Bisulphuret of platinum is insoluble both in hydrochloric acid and in nitric acid, but it dissolves readily in aqua regia.

4. *Hydrosulphuret of ammonia* produces the same precipitate, this redissolves completely in a large excess of the precipitant, if the latter contains an excess of sulphur in admixture. Acids reprecipitate the bisulphuret of platinum unaltered from this solution.

5. *Potass and Ammonia* produce in solutions of salts of platinum, when not too highly dilute, yellow chrystalline precipitates of POTASSIO-CHLORIDE OF PLATINUM and AMMONIO-CHLORIDE OF PLATINUM, which are insoluble in acids, but dissolve in an

excess of the precipitants, upon the application of heat. The presence of free hydrochloric acid promotes the precipitation greatly, since the acid effects the conversion of the free alkalies into chlorides.

6. *Protochloride of tin* fails to produce a precipitate in solutions of persalts of platinum which contain much free hydrochloric acid, but it simply imparts to them an INTENSELY DEEP BROWNISH-RED COLOR, owing to a reduction of the peroxide or bichloride of platinum, to protoxide or simple chloride.

Recapitulation and remarks.—The reactions of gold and platinum, or at least some of them, are sufficiently characteristic for the detection of these two metals, even though many other oxides be present, but more particularly to their individual detection when present in the same solution. Protochloride of tin and protoxide of iron are the most characteristic reagents for gold; potass and ammonia in presence of free hydrochloric acid, are the most positive tests for platinum, or, what comes to the same point, chloride of potassium and chloride of ammonium.

§ 95.

Second Section of the Sixth Group.

Special Reactions.

a. OXIDE OF ANTIMONY. ($Sb\,O_3$.)

1. The oxide of antimony presents, according to the mode of its preparation, either white, brilliant, crystalline needles, or a greyish white powder. It fuses at a gentle red heat, and when exposed to a higher temperature, volatilizes unaltered. It is insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acid. Oxide of antimony is readily reduced to the metallic state by fusion with cyanide of potassium.

2. Part of the salts of oxide of antimony are decomposed upon ignition; the haloid salts volatilize readily, and unaltered. The soluble neutral salts of antimony redden litmus paper. When

treated with a large amount of water, they are resolved into insoluble basic and soluble acid salts. Thus, for instance, water throws down from solutions of protochloride of antimony in hydrochloric acid, a white bulky precipitate of basic chloride of antimony (powder of Algaroth) $Sb\,Cl_3,\ 5\,Sb\,O_3$, which after some time becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and of course prevents its formation if mixed with the solution previously to the addition of the water. It is by this property that the basic protochloride of antimony is distinguished from the basic salts of bismuth formed under analogous circumstances.

3. *Sulphuretted hydrogen* precipitates from acid solutions of oxide of antimony, the whole of this metal, as orange-red PROTOSULPHURET OF ANTIMONY ($Sb\,S_3$). In alkaline solutions, this reagent fails to precipitate, or, at least, it fails to precipitate the whole of the antimony present; neutral solutions likewise are but imperfectly precipitated by sulphuretted hydrogen. The precipitated protosulphuret of antimony is readily redissolved by potass and by alkaline sulphurets, especially if the latter contain an excess of sulphur, whilst it is but scantily soluble in ammonia, and almost insoluble in bicarbonate of ammonia, that is, if the precipitate is free from any admixture of sulphur, and also of sulphantimonious and sulphantimonic acid. It is insoluble in dilute acids. Concentrated boiling hydrochloric acid dissolves it, with evolution of sulphuretted hydrogen gas. When heated in the air, it is converted into a mixture of antimonious acid with protosulphuret of antimony. When deflagrated with nitrate of potass, it yields sulphate of potass and antimoniate of potass. If a potass solution of protosulphuret of antimony be boiled with oxide of copper, sulphuret of copper will precipitate, and oxide of antimony dissolved in potass will remain in solution. If sulphuret of antimony be fused in conjunction with cyanide of potassium, metallic antimony and sulphocyanide of potassium will be produced. If the operation be conducted in a small tube ex-

panded into a bulb at the lower end, or in a stream of carbonic acid gas (vide § 95. *d.* 10) no sublimate of antimony will be produced. But if a mixture of sulphuret of antimony with carbonate of soda, or of cyanide of potassium and carbonate of soda, be heated in a glass tube, in a stream of hydrogen, (compare § 95. *d.* 3.) a mirror of antimony will be deposited on the inner surface of the tube, close behind the spot occupied by the mixture.

4. *Hydrosulphuret of ammonia* produces an orange-red precipitate of PROTOSULPHURET OF ANTIMONY, which redissolves readily in an excess of the precipitant, if the latter contains an excess of sulphur. Acids re-precipitate the protosulphuret of antimony unaltered from this solution; but this second precipitate contains an admixture of sulphur which makes its color appear somewhat lighter than that of the first.

5. *Potass*, *ammonia*, *carbonate of potass*, and *carbonate of ammonia*, throw down from the solutions of protochloride of antimony, also from solutions of simple salts of antimony,—but not, at least, not immediately, from solutions of tartar emetic or analogous compounds,—a white and bulky precipitate of OXIDE OF ANTIMONY, which redissolves readily in an excess of potass, but requires the application of heat for its re-solution in carbonate of potass or carbonate of ammonia, and is altogether insoluble in an excess of ammonia.

6. *Metallic zinc* precipitates from all solutions of oxide of antimony, unless containing free nitric acid, METALLIC ANTIMONY as a black powder. Should the solution under examination contain free nitric acid, oxide of antimony will precipitate in conjunction with the metal.

7. When a solution of oxide of antimony is brought into contact with *zinc* and *sulphuric acid*, the zinc oxidizes not only at the expense of the oxygen of the water, but also at the expense of that of the oxide of antimony, and the antimony separates in a metallic state; but a portion of the metal combines in the moment of its separation with the liberated hydrogen of the water. ANTIMONIURETTED HYDROGEN ($Sb\ H_3$.) If this operation be conducted in a gas-evolution flask, connected

by means of a perforated cork with the one limb of a bent tube, of which the other limb ends in a finely drawn-out point, pinched off at the top,* and the hydrogen passing through the fine aperture of the tube, be kindled, after all atmospheric air has been previously expelled, the flame will appear of a bluish-green tint, which is imparted to it by the antimony separating in a state of intense ignition upon the combustion of the antimoniuretted hydrogen; white fumes of oxide of antimony rise from the flame, which condense readily upon cold substances, and are not dissolved by water. If a cold substance (such as a porcelain plate) be now depressed upon the flame, METALLIC ANTIMONY will be deposited upon the surface of the plate, in a state of the most minute division, forming a deep black and almost lustreless spot. If the tube through which the gas is passing be heated to redness, in the centre, the bluish-green tint of the flame will decrease in intensity, and a metallic mirror of antimony of silvery lustre will form within the tube on both sides of the ignited part. If a stream of dry sulphuretted hydrogen be now very slowly transmitted through this tube, and the mirror be heated by means of a simple spirit-lamp, proceeding from its outer towards its inner extremity, that is, in an opposite direction to that of the gas stream, the mirror of antimony will become converted into sulphuret of antimony, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of dry hydrochloric acid gas be transmitted through the same glass tube, the sulphuret of antimony will disappear immediately, when present in thin layers only, and, after a few seconds, when the incrustation is somewhat thicker. The reason for this is, that the sulphuret of antimony transposes readily with hydrochloric acid, and the protochloride of antimony formed is exceedingly volatile in a stream of hydrochloric acid gas. If this gas stream be now transmitted through water, the presence of antimony in the latter may readily be proved by means of sulphuretted hydrogen. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals.

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* In accurate and precise experiments it is necessary to transmit the gas first through another tube, loosely filled with cotton, to prevent any moisture being carried into the final exit tube. Compare the engraving of Marsh's apparatus, § 95. *d*. 8.

8. If compounds of antimony, mixed with *carbonate of soda and cyanide of potassium*, be exposed on a charcoal support, to the *reducing flame of the blow-pipe*, brittle globules of METALLIC ANTIMONY will be produced, attended with volatilization of the reduced and reoxidized metal, which continues still some time after the removal of the sample from the flame, and is more particularly manifest when a stream of air is directed, by means of the blow-pipe, upon the surface of the cooling mass. The oxide of antimony formed is partly deposited on the charcoal as a white crust, and partly surrounds the metallic globules in the form of fine crystalline needles.

b. PROTOXIDE OF TIN. (SnO.)

1. Protoxide of tin is a black or greyish-black powder; its hydrate is white. Protoxide of tin is readily reduced by fusion with cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into peroxide of tin, which is insoluble in an excess of the acid.

2. The protosalts of tin are colorless, and are decomposed by heat. The soluble salts in the neutral state redden litmus paper. The addition of water to solutions of neutral protosalts of tin produces turbidity and milkiness in them; this is owing to the re-solution of the neutral salt into a soluble acid, and an insoluble basic salt; the solution clears again upon addition of hydrochloric acid.

3. *Sulphuretted hydrogen* throws down from neutral and acid solutions of protosalts of tin a dark brown precipitate of PROTOSULPHURET OF TIN, (SnS,) which is soluble in potass and in alkaline sulphurets, especially in those of the higher class, and equally so in concentrated boiling hydrochloric acid. Boiling nitric acid converts it into insoluble peroxide of tin. Alkaline

solutions of protosalts of tin are not, or, at any rate, but imperfectly precipitated by sulphuretted hydrogen.

4. *Hydrosulphuret of ammonia* produces the same precipitate of SULPHURET OF TIN. This precipitate redissolves with very great difficulty in an excess of the precipitant; but it redissolves readily in hydrosulphuret of ammonia containing an excess of sulphur, (which may be at once seen by the yellow color of the reagent,) or to which a small amount of finely-levigated sulphur has been added. From this solution in sulphuretted hydrosulphuret of ammonia, acids precipitate yellow bisulphuret of tin in conjunction with sulphur.

5. *Potass*, *ammonia*, *carbonate of potass*, and *carbonate of ammonia*, produce a white and bulky precipitate of HYDRATED PROTOXIDE OF TIN, ($Sn\,O,\ H\,O$,) which redissolves readily in an excess of potass, but is insoluble in an excess of the other three precipitants. Upon heating a concentrated solution of the hydrated protoxide of tin in potass, the protoxide is resolved into peroxide, which remains in solution, and metallic tin, which separates in the form of brown flakes.

6. *Perchloride of gold* produces in solutions of protochloride or protoxide of tin, upon the addition of some nitric acid, (without application of heat), a precipitate or coloration of PURPLE OF CASSIUS, (compare § 94, *a.*, 7.)

7. Solution of *perchloride of mercury*, when added in excess, produces in solutions of protochloride or protoxide of tin, a white precipitate of PROTOCHLORIDE OF MERCURY, owing to the protosalt of tin withdrawing from the perchloride of mercury one half of its chlorine.

8. If proto-compounds of tin be mixed with *carbonate of soda* and some *borax*, or, better still, with equal parts of *carbonate of soda* and *cyanide of potassium*, and the mixture be subsequently exposed on a charcoal support to the *inner blow-pipe flame*, ductile grains of METALLIC TIN will be obtained, unattended with any incrustation of the charcoal. The best way of freeing these grains of metallic tin from the surrounding particles of charcoal,

is to triturate the whole mass with water, in a small mortar—(in which operation some force should be used)—and to wash subsequently the charcoal powder off from the metallic particles.

c. PEROXIDE OF TIN. ($Sn O_2$.)

1. Peroxide of tin exists in two modifications which present a different deportment with solvents. The peroxide precipitated from persalts of tin by alkalies, is readily soluble both in potass and acids, but the peroxide produced by the oxidation of metallic tin with nitric acid is insoluble in potass and acids, the precipitated peroxide also becomes insoluble upon ignition. The insoluble modification is rendered soluble by fusion with carbonate of soda.

2. The persalts of tin are colorless, and are decomposed at a red-heat. The soluble persalts of tin in the neutral state redden litmus paper.

3. *Sulphuretted hydrogen* throws down, from acid and neutral solutions, a yellow precipitate of BISULPHURET OF TIN, ($Sn S_2$.) The application of heat promotes the formation of this precipitate. Alkaline solutions are not precipitated by this reagent. The bisulphuret of tin dissolves readily in potass, alkaline sulphurets, and concentrated boiling hydrochloric acid. It dissolves with difficulty in pure ammonia and in carbonate of ammonia. Nitric acid converts it into insoluble peroxide of tin. Upon deflagrating bisulphuret of tin with nitrate of potass, sulphate of potass and stannate of potass are produced. When a solution of bisulphuret of tin in potass is boiled with oxide of copper, sulphuret of copper and peroxide of tin are formed, the latter substance remaining dissolved in the potass solution.

4. *Hydrosulphuret of ammonia* produces the same precipitate of BISULPHURET OF TIN, which redissolves readily in an excess of the precipitant. From this solution acids reprecipitate the bisulphuret of tin unaltered.

5. *Potass* and *ammonia*, *carbonate of potass*, and *carbonate of ammonia*, precipitate white HYDRATED PEROXIDE OF TIN, (Sn

O_2, H O,) which redissolves readily in an excess of potass. It is more sparingly soluble in ammonia, and most so in alkaline carbonates.

6. *Metallic zinc* precipitates from solutions of perchloride or persalts of tin, which contain no free nitric acid, METALLIC TIN in the shape of small grey scales, or as a spongy mass. Should free nitric acid be present in the solution under examination, white HYDRATED PEROXIDE OF TIN will precipitate instead, or a mixture of metallic tin with hydrated peroxide.

7. The compounds of the peroxide of tin manifest the same deportment before the blow-pipe as the proto-compounds.

d. ARSENIOUS ACID. ($As\,O_3$.)

1. Arsenious acid appears generally either as a transparent vitreous, or as a white porcelain-like mass; when levigated, it forms a heavy white powder; when heated, it volatilizes in white inodorous fumes. It is difficultly soluble in cold, but more readily so in hot water. Hydrochloric acid and potass dissolve it copiously.

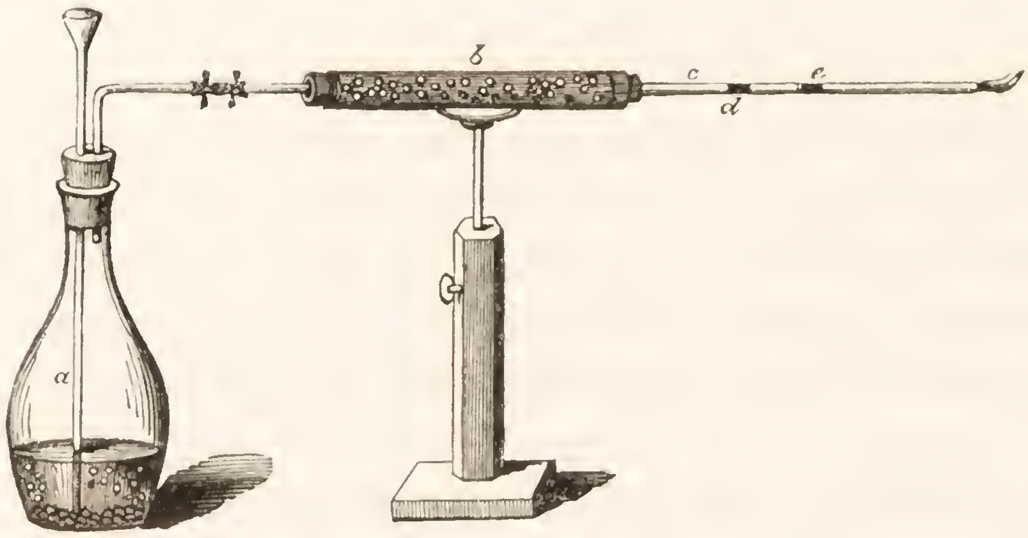
2. The arsenites are resolved upon ignition mostly into more fixed arseniates, and into metallic arsenic, which volatilizes. None of the arsenites, except those with alkaline bases, are soluble in water. The insoluble arsenites are dissolved, or, at least, decomposed by hydrochloric acid.

3. *Sulphuretted hydrogen* precipitates the solutions of arsenious acid and of neutral arsenites, slowly and imperfectly, except a free acid be present, when the precipitation will be immediate and perfect. Alkaline solutions are not precipitated. The precipitates are of a vividly yellow color; they consist of SULPHARSENIOUS ACID, ($As\,S_3$,) and are readily and completely redissolved by pure alkalies, alkaline carbonates, and bicarbonates, and likewise by alkaline sulphurets, but are nearly altogether insoluble in hydrochloric acid. Boiling nitric acid decomposes and dissolves sulpharsenious acid readily. The deflagration of sulpharsenious acid with carbonate of soda and nitrate of potass gives

rise to the formation of an alkaline arseniate and sulphate. When a solution of sulpharsenious acid in potass is boiled with oxide of copper, sulphuret of copper and arseniate of potass are formed. Upon boiling a similar solution with a hydrated carbonate or basic nitrate of bismuth, sulphuret of bismuth and arsenious acid are produced. If a mixture of sulpharsenious acid, with from three to four parts of carbonate of soda, and some water, to form it into a paste, be spread over some small glass splinters, and the latter, after having been well dried, rapidly heated to redness, in a glass tube, through which dry hydrogen gas is transmitted, the whole of the arsenic present will be reduced to the metallic state, and expelled. Part of the reduced arsenic forms a metallic mirror on the inner surface of the tube, the rest is carried away, suspended in the hydrogen gas; the suspended minute particles of arsenic impart a bluish tint to the flame of the hydrogen when kindled, and form stains of arsenic upon the surface of a porcelain plate depressed upon the flame. It is erroneous to suppose that arseniuretted hydrogen is formed in this process, although this might seem to be the case from the circumstance that, upon heating another part of the tube to redness, a fresh metallic mirror will be produced immediately behind the ignited place; but this is simply owing to the suspended particles of arsenic being reconverted into arseniacal fumes, which subsequently condense upon the cold part of the tube. That this is in reality the case, may be readily ascertained by conducting the hydrogen gas charged with the particles of arsenic, through water, and subsequently through a long tube, filled with moistened cotton; if this be done, pure hydrogen gas will escape from the emission tube, and all the arsenic will be retained by the water and the cotton in the form of a black powder. The fusion of two equivalents of sulpharsenious acid, with four equivalents of soda, gives rise at first to the formation of a double sulphuret of arsenic and sodium, and of arsenite of soda. Upon heating these products subsequently in hydrogen gas, the arsenious acid alone undergoes reduction, at first; but upon the application of a more intense heat, the sulpharsenious acid likewise is finally reduced to the metallic state. This method of reduction yields indeed very accurate results, but it does not enable us to distinguish arsenic from antimony with a sufficient degree of safety, nor to pronounce positively upon the presence or absence of arsenic in cases where antimony also happens to be present, (compare § 95, *a.*, 3.)

The operation is to be conducted in the apparatus illustrated by

PLATE IV.



a is the evolution flask, *b* a tube containing chloride of calcium, *c* the tube in which, at the point *d*, the glass splinter with the mixture of sulpharsenious acid and carbonate of soda is placed. As soon as the apparatus is completely filled with pure hydrogen gas, *d* is exposed at first to a gentle heat, in order to expel all the moisture which may still happen to be present, and then suddenly to a very intense heat, to prevent the sublimation of undecomposed sulphuret of arsenic. The metallic mirror is deposited near the point *e*; the sudden application of a very intense heat is best effected by means of the blow-pipe. A new method of effecting the reduction of sulphuret of arsenic to the metallic state, and which combines with the very highest degree of susceptibility this advantage, that it precludes the possibility of confounding arsenic with antimony, will be found described at § 95, *d.*, 10.

4. *Hydrosulphuret of ammonia* produces likewise a precipitate of SULPHARSENIOUS ACID. In neutral and alkaline solutions, however, the sulpharsenious acid, instead of precipitating, remains dissolved as a double sulphuret of arsenic and ammonium, but it precipitates from this solution immediately upon the addition of a free acid.

5. *Nitrate of silver* produces in neutral solutions of the arsenites, a yellow precipitate of ARSENITE OF SILVER, ($2\ Ag\ O,\ As\ O_3$,) which is soluble both in dilute nitric acid and in ammonia. *Ammonio-nitrate of silver* produces the same precipitate in solutions of arsenious acid, or of arsenites, when containing free acid.

6. *Sulphate of copper* and *ammonio-sulphate of copper* produce, under the same circumstances as the salts of silver, yellow-green precipitates of ARSENITE OF COPPER, ($2\ Cu\ O,\ As\ O_3$).

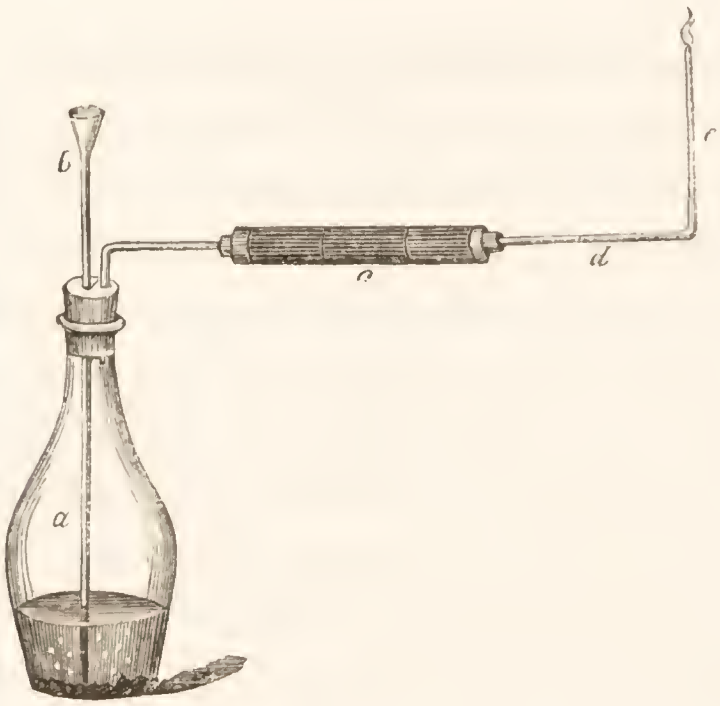
7. If to a solution of arsenious acid in an excess of *caustic potass ley,* or to the solution of an alkaline arsenite, mixed with *caustic potass,* a few drops of a dilute solution of sulphate copper be added, and the mixture subsequently boiled, a red precipitate of SUBOXIDE OF COPPER will fall down, and the solution will now contain arseniate of potass. This reaction is exceedingly delicate, provided a minute quantity only of solution of sulphate of copper be used. Even should the red precipitate of suboxide of copper be so exceedingly minute as to escape detection in transmitted light, yet it will be discernible still with great distinctness upon looking in at the top of the test tube. Of course this reaction, although of really great importance in certain instances, as a confirmatory proof of the presence of arsenious acid, and more particularly as a means of distinguishing arsenious acid from arsenic acid, is yet utterly inapplicable for the *direct detection* of arsenic, since grape sugar and other organic substances separate likewise and in the same manner suboxide of copper from salts of copper.

8. If an acid or neutral solution of arsenious acid, or of an arsenite, be mixed with *zinc, water,* and *sulphuric acid,* ARSE-

NIURETTED HYDROGEN ($As H_3$) will be formed, in the same manner as compounds of antimony, under analogous circumstances, yield antimoniuretted hydrogen. Compare § 95, *a*. 7. This deportment of arsenic affords us a most delicate test for the detection of this substance, and likewise a very valuable means to effect its isolation.

The process is invariably conducted in the apparatus illustrated by Plate V., and which has already been alluded to at § 95, *a*. 7. (Oxide of antimony.)

PLATE V.



a is the evolution flask, containing water and fragments of metallic zinc ; *b* is a funnel tube, through which the sulphuric acid, and subsequently the fluid to be tested for arsenic, are poured into the flask ; *c* is a glass tube, loosely filled with cotton, or, better still, with fragments of fused chloride of calcium, and to which a bent tube (*d e*) of DIFFICULTLY FUSIBLE glass, is fitted by means of a perforated cork ; the limb *c* of this tube is drawn out into a point, and pinched off at the top. When the evolution of hydrogen has proceeded for a considerable time, so that it may safely be concluded that all atmospheric air has been expelled from the apparatus, the gas is kindled at the aperture of the tube *d e*. (It is advisable to envelope the flask with a piece of cloth before kindling the gas, as an effectual means of preventing accidents should an explosion take place.) It is now absolutely necessary to ascertain, first, whether the zinc and the sulphuric acid are quite free from any admixture of arsenic. This is effected, 1st, by depressing a porcelain plate upon the flame; and, 2nd, by heating the central part of the tube *d e* to redness, for which purpose the limb *e* is to be turned into a horizontal position. If no incrustation appear, either on the plate or within the tube, this may be considered a proof of the perfect purity of the zinc and sulphuric acid from the slightest admixture of arsenic. The fluid to be tested is then introduced into the flask through the funnel tube. Should it contain arsenic, arseniuretted hydrogen will be evolved in conjunction with the hydrogen; and this arseniuretted hydrogen will impart a bluish tint to the flame, owing to the separation and ignition of the arsenic in the flame. At the same time white fumes of arsenious acid arise from the flame, which condense upon cold objects. If a porcelain plate be now depressed upon the flame, the separated and not yet reoxidized arsenic will condense upon the plate in the form of black spots. (Vide antimony, § 95, *a.* 7.) The spots formed by arsenic are of a rather blackish-brown color, and bright metallic lustre; whilst those of antimony are of a deep black color, and but feebly lustrous. If the central part of the limb *d* be heated to redness, the arsenic will condense in the cold part of the tube, forming a particularly beautiful and distinct metallic mirror, which is of darker and less silvery white hue than that formed by antimony under similar circumstances, and may be, moreover, distinguished from the latter by the characteristic odor of garlic, which becomes manifest upon cutting the tube off close to the mirror, and volatilizing the latter in the air, by the application of heat. Should the formation of metallic spots upon the porcelain plate seem to indicate the presence of arsenic, it will be necessary still to ascertain beyond the possibility of a doubt whether these spots consist in reality of arsenic and not of antimony; for even the characteristic odor of garlic is not sufficient to set at rest every doubt upon this point. The following methods are best adapted to lead to a positive conviction in this respect.

a. The central part of the tube through which the arseniuretted hydrogen passes, is heated to redness to produce a distinct metallic mirror. A very feeble stream of dry sulphuretted hydrogen is then transmitted through the tube, and the metallic mirror heated by means of a spirit-lamp, from its outer towards its inner extremity. If arsenic alone be present, yellow sulphuret of arsenic will be formed within the tube; if antimony alone be present, an orange or black sulphuret of antimony will be produced; but if the mirror consist of both metals jointly, the two sulphurets will appear side by side, the sulphuret of arsenic as the more volatile, lying invariably before the sulphuret of antimony. Not long ago, this conversion of antimony and arsenic into sulphurets was suggested as the surest means of distinguishing these two metals from one another. Experience has, however, taught us that the differences which the two sulphurets exhibit in color and volatility are not striking enough to prevent the possibility of mistakes. But if dry hydrochloric acid gas be now transmitted through the tube (containing the sulphuret of arsenic or sulphuret of antimony, or both sulphurets together) without application of heat, no alteration whatever will take place if sulphuret of arsenic alone is present, even though the gas be transmitted through the tube for a considerable time. If sulphuret of antimony alone is present, this will entirely disappear, and if both sulphurets are present, the sulphuret of antimony will immediately volatilize, whilst the yellow sulphuret of arsenic will remain. If a small quantity of ammonia be then introduced into the tube, the sulphuret of arsenic will be dissolved, and may thus be readily distinguished from sulphur which perhaps may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

b. The limb *c* is turned into an horizontal position, and the gas kindled and made to burn in a glass flask, having a capacity of about twelve ounces. This flask is placed in a beaker glass filled with cold water, and is constantly kept turning to prevent its becoming hot. After some time, when the oxygen in the flask is nearly exhausted, and the flame grows feeble, another flask is substituted for the first, and a third subsequently for the second, &c. &c. These flasks contain now, either arsenious acid alone, or oxide of antimony alone, or a mixture of both substances. If the first be the case, the white sublimate obtained will completely dissolve in hot water, and the solution may then be tested with other appropriate reagents to confirm the presence of arsenic. In the second case nothing will dissolve, nor in the third, if the oxide of antimony is present in sufficient quantity, since in that case arsenite of antimony will be formed. The arsenic in this last case may be detected by dissolving the sublimate in a small portion of dilute solution of potass, and adding to the solution sulphuretted hydrogen, and subsequently bicarbonate of ammonia in excess. Upon this, the whole of the antimony will precipitate as sulphuret of antimony, whilst the sulphuret of arsenic remains dissolved in the excess of bicarbonate of ammonia, whence it precipitates upon the addition of hydrochloric acid to acid reaction. This method is inferior to that described sub *a.*—Marsh was the first who suggested the method of detecting arsenic by the production of arseniuretted hydrogen.

9. If a perfectly dry mixture of arsenious acid, or an arsenite with *carbonate of soda and charcoal* be introduced into a well-dried glass tube, drawn out and closed at one end, and then heated to redness over a spirit-lamp, proceeding from the commencement of the small part towards the closed extremity, the charcoal will oxidize at the expense of the oxygen of the arsenious acid, and arsenic will be liberated, which volatilizes and re-condenses above the heated part of the tube, forming a more or less dark-brown metallic mirror of great lustre. This mirror may be driven further along in the tube by heat, and may thus finally be altogether expelled when, upon its volatilization in the air, the

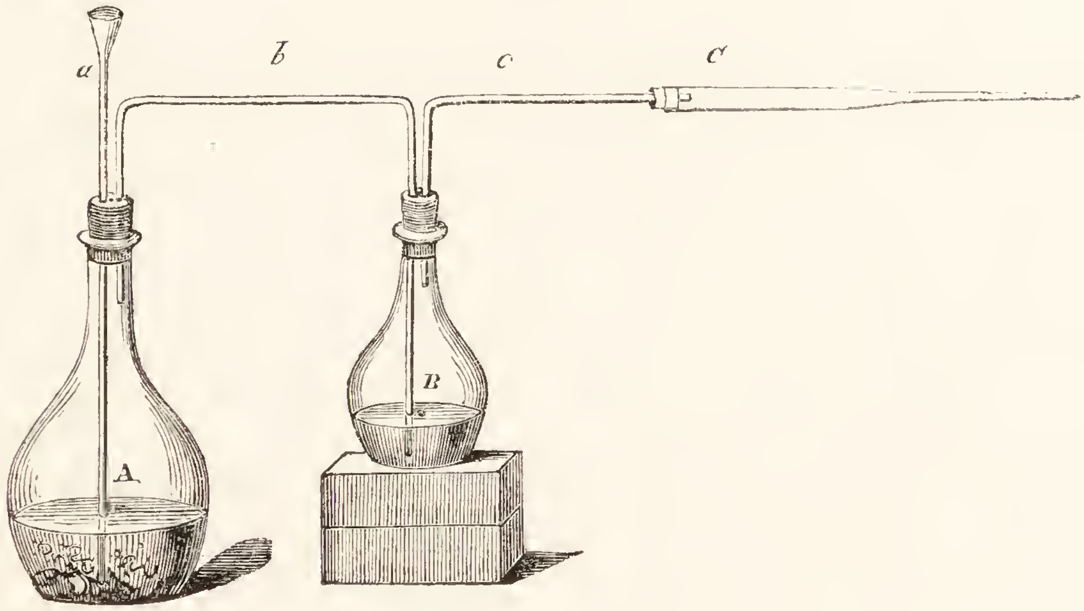
characteristic odor of arsenic will afford further confirmation of the presence of this substance. For the reduction of free arsenious acid, a fragment of charcoal is used, instead of carbonate of soda and charcoal; the arsenious acid is introduced into the drawn-out point of the tube, the fragment of charcoal is pushed over it and ignited, and heat is then applied to the point of the tube. This process has this advantage over the former, that charcoal is less likely to soil the tube than carbonate of soda and charcoal. The non-formation of a metallic mirror, when testing a supposed arsenite with carbonate of soda and charcoal, is not always a positive proof that no arsenic is present, since there are several compounds of arsenious acid, and more particularly those with heavy metallic oxides, e. g. peroxide of iron, which do not yield distinct metallic mirrors; it is therefore necessary to ascertain first, whether the arsenite in question may not belong to the latter class, before the non-formation of a mirror can be considered as a positive proof of the absence of arsenic.

10. Upon fusing arsenious acid, or arsenites, or a sulphuret of arsenic with a mixture of equal parts of dry *carbonate of soda* and *cyanide of* potassium, the whole of the arsenic is invariably reduced to the metallic state, and so are the others easily reduceable bases; the eliminated oxygen converts part of the cyanide of potassium into cyanate of potass—the eliminated sulphur (in the case of sulphurets of arsenic) converts the cyanide into sulphocyanide of potassium. The operation is conducted as follows:—the arsenical compound under examination is introduced, in a state of perfect dryness, into a small glass tube, expanded into a bulb at one end, and then covered with six times its quantity of the dry mixture of carbonate of soda and cyanide of potassium. The whole mass must not fill more than half the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. The heat of a spirit-lamp is then applied to the bulb, and maintained for a while, since the arsenic frequently requires some time for its complete sublimation. The mirrors which are obtained in this process are of exceeding purity. They are produced from all

arsenites, the bases of which remain either altogether unreduced, or are converted into metallic arseniurets, which lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity, neatness, and cleanness, as well as for the preciseness of the results attainable by its application, even though but minute quantities of arsenic be present. It is more especially adapted for the direct production of arsenic from sulphuret of arsenic, and is in this respect superior to all other methods hitherto suggested. The susceptibility of this method may be heightened exceedingly by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by Dr. BABO and myself, has shown that the most accurate and satisfactory results are to be obtained in the following manner:—

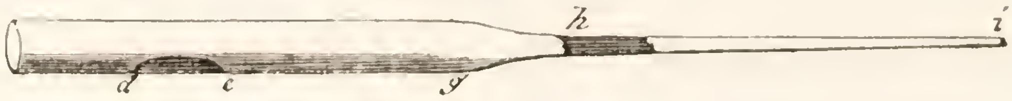
Plates VI. and VII. illustrate the apparatus in which the process is conducted.

PLATE VI.



A. is a capacious flask intended for the evolution of carbonic acid; it is half filled with water and large fragments of limestone or marble—(chalk does not yield a constant stream of carbonic acid gas.)—B is a smaller flask containing hydrated sulphuric acid. The flask A. is closed with a doubly perforated cork, into the one aperture of which is inserted a funnel-tube (*a*) which reaches nearly to the bottom of the flask; into the other perforation is fitted a tube (*b*) which serves to conduct the evolved gas into the hydrate sulphuric acid in B, when it is thoroughly freed from moisture. The tube *c*. conducts the dried gas into the reduction tube C, which is illustrated by

PLATE VII.



This engraving represents the tube on the scale of one-third of its length. When the apparatus is arranged, the perfectly dry sulphuret of arsenic, or arsenite under examination, is to be triturated in a slightly heated mortar with about 12 parts of a dry mixture, consisting of 3 parts of carbonate of soda and 1 part of cyanide of potassium. The powder is placed upon a narrow slip of card paper bent into the shape of a gutter, and the latter is then pushed into the reduction tube up to *e*; by turning the tube half-way round its axis, the mixture is made to fall down into the tube between *e* and *d*, every other part of the tube remaining perfectly clean. The tube thus prepared is now connected with the gas evolution apparatus, and a moderate stream of carbonic acid is then evolved by pouring some hydrochloric acid into the funnel-tube *a*. The mixture in *e* is now most carefully and thoroughly dried by heating the tube its whole length very gently with a spirit-lamp. When every trace of water is expelled, and the gas-stream has become so slow that the single bubbles pass through the sulphuric acid in B. at intervals of one second, the reduction-tube is heated to redness at *g*, by means of a spirit-lamp; as soon as *g* is red hot, the flame of a second and larger spirit-lamp is applied to the mixture, proceeding from *d* to *e* until the whole of the arsenic is reduced and volatilized. The far greater portion of the volatilized arsenic recondenses at *h*, whilst an extremely minute portion only escapes through *i*, imparting to the surrounding air the peculiar odor of garlic. The flame of the second lamp is finally slowly and gradually advanced up to *g*, and by this means the whole of the arsenic which may have condensed in the wide part of the tube, is propelled to *h*. When this has been attained, the tube is closed at the point *i* by fusion, and the mirror is then finally driven by the application of heat from *i* towards *h*. In this manner, perfectly distinct metallic mirrors may be produced from as little as the 1-300th part of one grain of sulphuret of arsenic. Neither sulphuret of antimony nor any other compound of antimony yield metallic mirrors, when treated in this manner.

11. If to arsenious acid (in the solid form or solution) some *acetic acid* be added, and subsequently an excess of potass, the mixture evaporated to dryness, and the residue finally ignited in a small tube, ALCARSIN (Oxide of cacodyl. $C_4 H_6 As+O$) will be formed, which may be at once detected by its characteristic and insupportable odor. This odor changes immediately to the no less characteristic odor of chloride of cacodyl, when the ignited contents of the tube are mixed with a few drops of protochloride of tin, and are then again exposed to the action of heat. This deportment of arsenious acid affords us likewise a means of determining whether metallic mirrors obtained by Marsh's apparatus, are really arsenical mirrors or not. For this purpose, the metallic crust which it is intended to examine, is boiled with water impregnated with atmospheric air until it is completely dissolved; the solution is mixed with acetic acid and an excess of potass; the mixture is evaporated to dryness, and the residue subsequently ignited in a small tube—in short, the whole process is conducted as I have just now described. BUNSEN has recently suggested this method of testing arsenical crusts; it should be borne in mind, however, that these crusts dissolve but very slowly upon boiling with the aerated water.

12. If arsenious acid or an arsenite be exposed on a charcoal support to the *reducing flame of the blow-pipe*, a highly characteristic garlic odor will be perceived, especially if some car-

bonate of soda be added to the substance examined. This odor has its origin in the reduction and reoxidation of the arsenic, and enables us to detect very minute quantities. This test, however, is not to be implicitly relied upon. The garlic odor proceeds neither from the fumes of arsenious acid, nor from those of arsenic, but probably from those of a lower degree of oxidation of the latter substance. Arsenic exhales this odor invariably when heated in the air.

e. ARSENIC ACID. ($As\ O_5$.)

1. Arsenic acid is a colorless, or white mass, which deliquesces gradually in the air, and dissolves in water; it fuses at a gentle red-heat without suffering decomposition; but at a higher temperature it is resolved into oxygen and arsenious acid, which volatilizes.

2. Most of the arseniates are insoluble in water. Of the neutral arseniates, those with alkaline bases alone are soluble in water. Most of the neutral and basic arseniates can bear a strong red-heat without suffering decomposition. The acid arseniates lose their excess of acid upon ignition, this excess being resolved into arsenious acid and oxygen.

3. *Sulphuretted hydrogen* fails to precipitate alkaline and neutral solutions of arseniates; but in acidified solutions it produces a yellow precipitate of SULPHARSENIC ACID, ($As.\ S_5$.) This precipitate never forms instantaneously, and in dilute solutions frequently only after the lapse of a considerable time (twenty-four hours). Heat promotes its separation. The sulpharsenic acid manifests the same deportment as the sulpharsenious acid, with the various solvents and decomposing agents which I have mentioned while treating of the latter substance. Sulphurous acid, when added to a solution of free arsenic acid or of an arseniate, transposes with the arsenic acid, to arsenious acid and sulphuric acid; this process of transposition may be promoted by the application of heat. If sulphuretted hydrogen, and should this be

required, an acid be now added to the mixture, the whole of the arsenic will immediately precipitate as sulpharsenious acid.

4. *Hydrosulphuret of ammonia* converts the arsenic acid in neutral and alkaline solutions of arseniates into sulpharsenic acid, which remains in solution as sulpharsenico-sulphuret of ammonium. Upon the addition of an acid to the solution, this double sulphuret is decomposed, and sulpharsenic acid precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions are precipitated with sulphuretted hydrogen. It is promoted by heat.

5. *Nitrate of silver* produces in neutral solutions of the arseniates highly characteristic reddish-brown precipitates of ARSENIATE OF SILVER, ($3\,Ag\,O, As\,O_5$,) which are soluble both in dilute nitric acid and in ammonia. *Ammonio-nitrate of silver* produces the same precipitate in solutions of arsenic acid or of arseniates, when containing a free acid.

6. *Sulphate of copper* and *ammonio-sulphate of copper* produce, under the same circumstances as the nitrate and ammonio-nitrate of silver, greenish blue precipitates of ARSENIATE OF COPPER. ($As\,O_5, 2\,Cu\,O, H\,O$.)

7. With *hydrogen, carbonate of soda, and charcoal, cyanide of potassium,* and before the *blow-pipe,* the arseniates manifest the same deportment as the arsenites.

Recapitulation and remarks.—The separation and positive detection of the oxides belonging to the second section of the sixth group, and especially of peroxide of tin, are sometimes, and under certain circumstances, attended with difficulties. The protoxide of tin, however, may be readily detected by its reaction with perchloride of gold, or with perchloride of mercury, even in the presence of other oxides. The separation of peroxide of tin from oxide of antimony may be effected with tolerable accuracy in the humid way by means of a hot solution of bitartrate of potass, or of a solution of free tartaric acid; but this method is applied with success only when the peroxide of tin exists in the modification produced by the action of nitric acid on metallic tin. It is necessary, therefore, if the substance under examination is not an alloy, to reduce the compound of tin to the metallic state, either in the humid way, by means of zinc, the presence of nitric acid being carefully avoided—or, in the dry way, by means of cyanide of potassium. The method of separating antimony from tin in the form of sulphurets, by means of ammonia, is always liable to give rise to mistakes, since the higher sulphurets of antimony are soluble in ammonia, and even the protosulphuret of this metal is not quite insoluble in this substance. The only *positive* proof of the presence of peroxide of tin is the production of a *ductile* metallic grain of tin, in the reducing flame of the blow-pipe, since the ductility of tin distinguishes this metal amply and sufficiently from antimony. This reduction is very readily effected before the blow-pipe by means of a mixture of equal parts of cyanide of potassium and carbonate of soda; but care should be taken that the peroxide of tin be not mixed with nitre—since this would cause deflagration—nor with any other substance of that description. Whether the ductile metallic grain produced in the process be *really* tin may be ascertained and confirmed by the following direct experiment;—the metallic grain is boiled with some concentrated hydrochloric acid, water is subsequently added to the solution, and the fluid finally tested with perchloride of mercury. Vide § 95. *b*. 7.

Peroxide of tin and oxide of antimony may also be detected and distinguished, side by side, before the blow-pipe, since the antimony is characterized by the peculiar incrustation with which its oxide covers the charcoal support, and since the peroxide of tin, after the volatilization of the antimony, may be readily recognized by the ductility of the grain of metallic tin produced in the process, as I have just stated. I have, however, found that inexperienced students fail generally in their attempts at detecting peroxide of tin and oxide of antimony, side by side, in this manner. Antimony may be recognized, moreover, by the decomposition which its chloride suffers by the action of water, and likewise by the color of its sulphuret. The latter test, however, is uncertain, if the sulphuret of antimony happens to contain much sulphuret of arsenic in admixture. The best way of arriving at a positive conclusion in such cases is to ignite the mixed sulphurets,—when the sulphuret of arsenic will volatilize to dissolve the residue in hydrochloric acid, and to test the solution again with sulphuretted hydrogen.

The detection of arsenic is not difficult, yet, nevertheless, errors will frequently arise, especially if positive and definite conclusions be drawn from individual and isolated reactions, such as the characteristic odor, for instance, which arsenical compounds exhale when heated on charcoal. We must, therefore, lay it down as a rule that the presence of arsenic is to be considered positively proved only by a concurrence of the various reactions, and particularly by the production of metallic arsenic.—Arsenic may be separated from tin with tolerable accuracy by deflagrating the sulphurets of the two metals with carbonate of soda and nitre. The presence of tin, moreover, does not interfere with the detection of arsenic. But the case is very different with antimony, especially when testing by Marsh's method, which is now so universally adopted. The mere production of a metallic mirror by Marsh's apparatus ought, therefore, never to be looked upon as a positive proof of the presence of arsenic, and additional tests must invariably be had recourse to, to place the presence of this substance beyond all doubt. The method described at § 95. *d.* 8. *a.*, yields the most positive and precise results in this respect, and is, moreover, exceedingly delicate. A tolerably complete separation of arsenic from antimony may be effected by means of bicarbonate of ammonia, the protosulphuret of antimony being nearly altogether insoluble in this substance, whilst the sulphuret of arsenic dissolves readily in it. But this method of distinguishing between arsenic and antimony yields precise results only when the protosulphuret of antimony is entirely free from any admixture of a higher sulphuret or of free sulphur, and when the proportion of sulphuret of arsenic present is not too inconsiderable. It is, therefore, generally inapplicable for the separation of the sulphurets produced in the usual way.

Those methods of effecting the separation of arsenic from antimony, which are based upon the different deportment of the respective sulphurets of the two metals, with concentrated hydrochloric acid, or with caustic ammonia, yield even less precise results than the method just now described; nor is the perfect separation of the two metals to be effected by dissolving the sulphurets in potass, and boiling the solution with oxide of copper. A far more precise result may be obtained by deflagrating the sulphurets with carbonate of soda and nitre, treating the residuary mass with water, filtering the solution, and decomposing subsequently with nitric acid, the small quantity of basic antimoniated alkali present in the filtrate. Nearly the whole of the antimony is obtained in this process, as an insoluble, and the whole of the arsenic as a soluble compound.

The presence of antimony does not interfere with the accuracy of the results obtained by the reduction of arsenites or arseniates, by means of *carbonate of soda and charcoal*, or by means of *cyanide of potassium* and *carbonate of soda*. Arsenious acid and arsenic acid in aqueous solution may be most readily and positively distinguished from one another, by means of nitrate of silver. Should the presence of other substances interfere with the direct application of the test, the solution is to be precipitated completely with sulphuretted hydrogen; the precipitated sulphurets are then to be dissolved in potass ley, and the solution is subsequently to be boiled either with hydrated oxide or carbonate, or basic nitrate of bismuth; the fluid is then to be filtered off from the precipitated sulphuret of bismuth, and one portion of the filtrate tested for arsenious acid by means of sulphate of copper, according to the method described § 95. *d.* 7; another portion of the filtrate is to be neutralized with nitric acid, and finally tested for arsenic acid, by means of nitrate of silver.

B. DEPORTMENT OF THE ACIDS WITH REAGENTS.

§ 96.

We classify the reagents which serve for the determination of the acids, in the same manner as those used for the determination of the bases, into GENERAL REAGENTS, i. e. such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, i. e. such as serve to effect the detection of the INDIVIDUAL ACIDS. The groups into which we classify the various acids can scarcely be defined and limited with the same degree of preciseness as the groups into which the bases are divided.

The two principal groups into which acids are divided are that of INORGANIC and that of ORGANIC ACIDS. It is, however, by no means easy to select a general property equally applicable and characteristic throughout the entire series; for we can neither adopt the ternary composition as a distinguishing mark of organic acids, without excluding oxalic acid, for instance, nor can we define organic acids to be such as require for their formation the co-operation of the vital power, since such a definition would not only be wanting in precision with regard to a great many acids, such as formic acid, succinic acid, &c., but must, moreover, be looked upon as altogether unscientific, since all the vital processes in the animal and vegetable body are simply in fact modified chemical processes. We will, therefore, select here, as the characteristic mark to guide us in the classification into organic and inorganic acids, the deportment which the various acids manifest at a high temperature, and will therefore call *organic* those acids of which the salts—(particularly those which have an alkali or an alkaline earth for base)—are decomposed upon ignition, this decomposition being attended with separation of charcoal.

By selecting this deportment at a high temperature as the distinctive characteristic of organic acids, we are enabled to determine at once by a most simple preliminary experiment the class to which the acid or acids under examination belong. The salts of organic acids with alkalies or alkaline earths are converted into carbonates, upon ignition.

I. INORGANIC ACIDS.

First Group.

ACIDS WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY CHLORIDE OF BARIUM: *Arsenious Acid—Arsenic Acid—Chromic Acid—Sulphuric Acid—Phosphoric Acid—Boracic Acid—Oxalic Acid—Hydrofluoric Acid—Carbonic Acid—Silicic Acid.*

This group is again subdivided into four clasees, viz.:

1. Acids which are decomposed in acid solutions by sulphuretted hydrogen, and which have therefore been alluded to already, while treating of the bases, viz., ARSENIOUS ACID, ARSENIC ACID, and CHROMIC ACID.
2. Acids which are not decomposed in acid solutions by sulphuretted hydrogen, and the barytes compounds of which are insoluble in hydrochloric acid. Of the above enumerated acids SULPHURIC ACID alone belongs to this class.
3. Acids which are not decomposed in acid solutions, by sulphuretted hydrogen, and the barytes compounds of which dissolve in hydrochloric acid apparently WITHOUT DECOMPOSITION, inasmuch as the acids cannot be completely separated from the hydrochloric solution, by heating or evaporation; these are PHOSPHORIC ACID, BORACIC AICD, OXALIC ACID, and HYDROFLUORIC ACID. (Oxalic acid belongs more properly to the organic group. I add this acid, however, here to the inorganic class, since its salts are decomposed upon ignition without leaving a real carbonaceous residue, and are accord-

ingly liable to be confounded with the salts of inorganic acids.)

4. Acids which are not decomposed in acid solutions, by sulphuretted hydrogen, and the barytes salts of which are soluble in hydrochloric acid, WITH DECOMPOSITION, (separation of the acids:) CARBONIC ACID, SILICIC ACID.

First Section of the First Group of the Inorganic Acids.

§ 97.

a. Sulphuretted hydrogen precipitates from acid solutions of ARSENIOUS ACID and ARSENIC ACID, the corresponding sulphurets of these acids. Since this would lead to confounding them rather with the metallic oxides than with other acids, I deemed it more judicious to place these two acids with the oxides of the sixth group, (vide § 95).

b. CHROMIC ACID. ($Cr\,O_3$.)

1. Chromic acid forms a scarlet-red crystalline mass or distinct crystals presenting the form of needles. Upon ignition it is resolved into oxide of chromium and oxygen. It deliquesces rapidly when exposed to the air. It dissolves in water, imparting to this menstruum a deep red-brown tint, which remains visible even when considerably diluted.

2. The chromates are all red or yellow, and for the most part insoluble in water. Some of them are decomposed upon ignition; those with alkaline bases are fixed, and soluble in water; the solutions of the neutral alkaline chromates are yellow, those of the acid alkaline chromates are red. These tints are still visible in highly dilute solutions. The yellow color of a neutral solution changes into red on the addition of a mineral acid, owing to the formation of an acid salt.

3. *Sulphuretted hydrogen* reduces chromic acid, no matter whether present in solution in the free state or as a chromate;

oxide of chromium, water, and sulphuric acid, are formed in this process, and sulphur precipitates. Heat promotes this decomposition. When no free acid is present, a portion only of the reduced oxide of chromium is retained in solution by the new-formed sulphuric acid, and a greenish-grey precipitate is produced consisting of a mixture of hydrated oxide of chromium with sulphur. But if free acid is present, the precipitate is far less considerable and consists of pure sulphur. The salt of oxide of chromium formed imparts a green tint to the fluid, in either case.

4. Chromic acid may also be reduced to chromic oxide by means of many other substances besides sulphuretted hydrogen, more particularly by *sulphurous acid*, or by heating with *hydrochloric acid,* especially upon addition of alcohol, (when hydrochloric ether and aldehyde are evolved,) or also by *metallic zinc,* or by heating with *tartaric acid, oxalic acid,* &c. All these reactions are clearly characterized by the transition of the red or yellow color of the solution to the green tint of the reduced salt of oxide of chromium.

5. *Chloride of barium* produces a yellowish white precipitate of CHROMATE OF BARYTES ($Ba O, Cr O_3$) which is soluble in dilute hydrochloric and nitric acid.

6. *Nitrate of silver* produces a dark purple-red precipitate of CHROMATE OF SILVER ($Ag O, Cr O_3$) which is soluble in nitric acid and in ammonia.

7. *Acetate of lead* produces a yellow precipitate of CHROMATE OF LEAD ($Pb O, Cr O_3$) which is soluble in potass, and sparingly soluble in dilute nitric acid. The yellow color of this precipitate changes to red, upon heating with ammonia.

8. When insoluble chromates are fused with *carbonate of soda* and *nitre,* and the fused mass is subsequently treated with water, the fluid produced looks YELLOW from the alkaline chromate which it holds in solution; upon the addition of an acid, this yellow color changes to red. The oxides remain either in their pure state or as carbonates.

Remarks.—When testing for bases we always find the chromic acid as chromic oxide, since sulphuretted hydrogen reduces the acid to the state of oxide. The characteristic color of the solution frequently renders the application of any further test almost a work of supererogation. If there is reason to suppose that chromic acid is present in a solution, metallic oxides being likewise present, it is preferable to effect the reduction of the chromic acid, by means of hydrochloric acid and alcohol, or by means of sulphurous acid, instead of reducing it with sulphuretted hydrogen. The reactions with salts of silver and salts of lead afford a positive and confirmatory proof of the presence of chromic acid in aqueous solutions.

Second Section of the First Group of the Inorganic Acids.

§ 98.

SULPHURIC ACID. ($S\,O_3$.)

1. Anhydrous sulphuric acid is a white feathery-crystalline mass which emits strong fumes upon exposure to the air; hydrated sulphuric acid forms an oily liquid, colorless and pellucid like water. Both the anhydrous and hydrated acid carbonize organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature.

2. Most of the sulphates are soluble in water; the insoluble sulphates are generally white; the soluble sulphates are for the most part colorless, in their crystalline state. The sulphates of the alkalies and alkaline earths are not decomposed upon ignition.

3. *Chloride of barium* produces in even highly dilute solutions of sulphuric acid and of the sulphates, a heavy white precipitate of SULPHATE OF BARYTES ($Ba\,O, SO_3$) in form of a fine powder; this precipitate is insoluble in hydrochloric acid and in nitric acid.

4. *Acetate of lead* produces a heavy, white precipitate of SULPHATE OF LEAD ($Pb\,O, SO_3$) which is sparingly soluble in dilute

nitric acid, but dissolves completely in hot concentrated hydrochloric acid.

5. The salts of sulphuric acid with the alkaline earths which are insoluble in water and acids, are converted into CARBONATES by fusion with *alkaline carbonates.* But the sulphate of lead is reduced to the state of PURE OXIDE when treated in this manner. Both the conversion of the former into carbonates, and the reduction of the latter to the state of oxide, are attended with the formation of an alkaline sulphate.

6. Upon fusing sulphates with *carbonate of soda and charcoal,* on the loop of a platinum wire, in the inner flame of the blow-pipe, the sulphuric acid is reduced, and sulphuret of sodium formed, which may be readily recognized by the odor of sulphuretted hydrogen emitted by the button when moistened with some acid. If the process of moistening the button be performed upon a piece of paper imbued with solution of lead, or upon a clean silver plate, (such as a polished coin,) a black stain of sulphuret of lead or sulphuret of silver will immediately form upon the paper or coin.

Remarks.—The characteristic and exceedingly delicate reaction of sulphuric acid with salts of barytes renders the detection of this acid an easier task than that of almost any other acid. It is simply necessary to take care not to confound with sulphate of barytes, precipitates of chloride of barium, and particularly of nitrate of barytes, which are formed upon mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of barytes, since they redissolve immediately upon diluting the acid fluid with water. The deportment of sulphuric acid with barytes might, however, lead to confounding this acid with hydrofluosilicic acid. Although we do not treat of the latter substance in the present work, yet it may not be amiss to remark that, should any doubt arise as to a precipitate of barytes, this may be easily set at rest by fusing the precipitate in question in the inner flame of the blow-pipe, with carbonate of soda and charcoal. (Compare § 98. 6.)

Third Section of the First Group of the Inorganic Acids.

§ 99.

a. PHOSPHORIC ACID. (PO_5.)

We shall treat here only tribasic phosphoric acid, since it is this form of the acid and its salts which are used in pharmacy; monobasic and bibasic acids we pass by.

1. The hydrate of common phosphoric acid (PO_5, 3 HO) forms colorless and pellucid crystals which deliquesce rapidly in the air, forming a simply non-caustic fluid. The action of heat changes it into hydrated pyro, or meta-phosphoric acid, according as either one or two equivalents of water are expelled.

2. The action of heat fails to decompose the phosphates with fixed bases, but converts them into pyrophosphates when, containing one equivalent of basic water, and into metaphosphates, when containing two equivalents of basic water. The phosphates with alkaline bases alone are soluble in water in the neutral state. The solutions manifest alkaline reaction.

3. *Chloride of barium* produces in aqueous solutions of the neutral or basic phosphates, a white precipitate of PHOSPHATE OF BARYTES [PO_5, 2 Ba O, HO, or PO_5, 3 Ba O]* which is insoluble in hydrochloric acid and in nitric acid, and difficultly soluble in chloride of ammonium.

4. *Solution of gypsum* produces in neutral or alkaline solutions of phosphates, a white precipitate of PHOSPHATE OF LIME (PO_5, 2 Ca O, HO, or PO_5, 3 Ca O) which dissolves readily in acids, even in acetic acid.

5. *Chloride of magnesium* or *sulphate of magnesia* produce in

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* Precipitates of the former composition are formed in solutions containing an alkaline phosphate with two equivalents of fixed bases or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate, with three equivalents of fixed base or ammonia.

neutral solutions of phosphates white precipitates of PHOSPHATE OF MAGNESIA (PO_5, 2 Mg O, HO) which are, however, visible only in rather concentrated solutions, particularly upon the application of heat. But if *free ammonia* or *carbonate of ammonia* be added to the solution, the chloride of magnesium or sulphate of magnesia, will produce in even highly dilute solutions, a white, crystalline and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA (PO_5 2 Mg O, NH_4 O) which is insoluble both in ammonia and chloride of ammonium, but dissolves readily in acids, even in acetic acid. This precipitate appears often only after the lapse of some time; stirring and agitation promotes its separation, vide § 87. *d.* 7. In solutions of phosphates with three equivalents of fixed base, salts of magnesia, produce immediately a precipitate of basic phosphate of magnesia (PO_5, 3 Mg O,) and this even though the solution be dilute.

6. *Nitrate of silver* throws down from the solutions of neutral and basic alkaline phosphates, a light yellow precipitate of PHOSPHATE OF SILVER. (PO_5, 3 Ag O.) If the solution contained originally a basic phosphate, the fluid in which the precipitate is suspended, will manifest a neutral reaction, whilst the reaction will be acid, if the solution contained originally a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives for the three equivalents of oxide of silver, which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water, (the latter does not neutralize the acid properties of the nitric acid).

7. *Acetate of lead* produces in neutral and alkaline solutions of phosphates a white precipitate of PHOSPHATE OF LEAD, (PO_5, 3 Pb O) which is readily soluble in nitric acid, but nearly insoluble in acetic acid. This reaction acquires a very great value as a test for phosphoric acid, from the peculiar deportment which the precipitated phosphate of lead exhibits before the blow-pipe. For, in the first place, even the inner flame of the blow-pipe fails to reduce it, or effects its reduction only with the greatest difficulty, and, in the second place, the colorless and transparent button which it yields

in the oxidizing flame turns opaque upon cooling, and crystallizes generally into perfectly distinct dodecahedrons.

8. If to a solution containing phosphoric acid, no matter in whatever form or combination, hydrochloric acid be added to acid reaction, and subsequently one or two drops of *perchloride of iron*, and finally *acetate of potass* in excess, a floculent gelatinous white precipitate of *perphosphate of iron* ($3\,PO_5, 2\,Fe_2\,O_3, 3\,HO$) will be produced invariably and under all circumstances. Should more perchloride of iron have been added than corresponds to the amount of phosphoric acid present, the fluid in which the precipitate is suspended, will appear red; otherwise it will appear colorless. Should the quantity of phosphoric acid present be very minute, the precipitate will become distinctly visible only after from 12 to 24 hours' standing. This reaction is well adapted for the detection of phosphoric acid in general, and more particularly when we have to deal with acid solutions of phosphates of the alkaline earths. The perfect and complete separation of the alkaline earths from the phosphoric acid, is best effected by the following process. Hydrochloric acid is added to the solution of the phosphate under examination, until the fluid manifests an acid reaction, and as much perchloride of iron is then added as will cause the fluid to turn red upon the subsequent mixing with acetate of potass in excess; the mixture is then boiled, which will cause the whole of the peroxide of iron and phosphoric acid to precipitate; the fluid is then finally filtered off from the precipitate. The filtrate, which is colorless, contains the whole of the alkaline earths as chlorides.

b. BORACIC ACID. (BO_3.)

1. Boracic acid, in its anhydrous state, is a colorless glass, when hydrated it is a porous white mass; in the crystalline state it presents small scaly laminæ. It is soluble in water and alcohol;—the solutions redden litmus paper, but color turmeric paper brown. The borates are not decomposed upon ignition; those with alkaline bases alone are readily soluble in water. The solutions are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, when not too highly dilute, a white precipitate of BORATE OF BARYTES, ($Ba\,O,\ B\,O_3$,) which is soluble in acids and ammoniacal salts.

3. *Nitrate of silver* produces in rather concentrated solutions of borates, a white precipitate of BORATE OF SILVER, ($Ag\,O,\ B\,O_3$,) which is soluble in nitric acid, and in ammonia.

4. If *sulphuric acid* or *hydrochloric acid* be added to highly concentrated hot solutions of borates, the BORACIC ACID will separate upon cooling, in the form of shining crystalline scales.

5. If alcohol be poured over free boracic acid or a borate—(in which latter case the boracic acid is to be liberated by the addition of sulphuric acid, which should be used concentrated and in sufficient quantity)—and the mixture be subsequently ignited, the flame will appear of a very distinct YELLOWISH-GREEN color, especially upon stirring the mixture; this tint is owing to the ignition of the evaporating boracic acid, in its passage through the flame. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, igniting the alcohol, allowing it to burn for a short time, extinguishing the flame, and rekindling it. At the first flickering of the flame its borders will now appear green, even though the quantity of the boracic acid be so minute that it fails to produce a perceptible coloring of the flame, when treated in the usual manner.

c. OXALIC ACID. ($2\,C\,O+O=C_2\,O_3=\bar{O}$.)

1. The hydrate of oxalic acid is a white powder; the crystallized acid forms colorless rhombic columns. Both the hydrate and the crystallized acid dissolve readily in water and in alcohol. When heated rapidly in open vessels, part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating, and provoke coughing.

2. The whole of the oxalates undergo decomposition at a red-heat, the oxalic acid being resolved into carbonic acid and carbonic oxide. Those which have an alkali or an alkaline earth

for base, are in this process converted into carbonates (without separation of charcoal, when pure); those with metallic base leave either the pure metal or the oxide behind, according to the greater or less degree of reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. *Chloride of barium* produces in neutral solutions of oxalates, a white precipitate of OXALATE OF BARYTES, ($Ba\,O, \bar{O}$,) which is soluble in nitric acid and in hydrochloric acid, but dissolves more sparingly in ammoniacal salts than borate of barytes.

4. *Nitrate of silver* produces in neutral solutions of oxalates, a white precipitate of OXALATE OF SILVER, ($Ag\,O, \bar{O}$,) which is soluble in nitric acid and in ammonia.

5. *Lime-water*, and all the *soluble salts of lime*, and consequently *solution of gypsum*, produce in even highly dilute solutions of free oxalic acid or of oxalates, white pulverulent precipitates of OXALATE OF LIME, ($Ca\,O, \bar{O}$,) which dissolve readily in hydrochloric acid and in nitric acid, but are nearly insoluble in oxalic acid and in acetic acid. The presence of ammoniacal salts does not interfere with the formation of these precipitates. The addition of ammonia promotes the precipitation of the free oxalic acid by salts of lime.

6. When oxalic acid or an oxalate in a dry state is heated with an excess of *concentrated sulphuric acid*, the latter withdraws from the oxalic acid its constitutional water, and thus causes its resolution into CARBONIC ACID and CARBONIC OXIDE, ($C_2\,O_3 = C\,O + C\,O_2$,) which two gases escape with effervescence. If the quantity operated upon is not too minute, the escaping carbonic oxide gas may be kindled; it burns with a blue flame. Should the sulphuric acid acquire a dark tint in this reaction, this is a sign that the oxalic acid examined contained some organic substance in admixture.

d. HYDROFLUORIC ACID. ($Fl\,H.$)

1. Hydrofluoric acid is a colorless, highly volatile fluid of pungent odor; it emits fumes when exposed to the air, and is miscible with water in all proportions. Hydrofluoric acid is distinguished from all other acids by the exclusive property it possesses to dissolve the insoluble modification of silicic acid, and likewise those of the silicates which are insoluble in hydrochloric acid. Fluoride of silicon and water are formed in the process of solution.

$$(Si\,O_2 + 2\,Fl\,H = Si\,Fl_2 + 2\,H\,O.)$$

Hydrofluoric acid transposes with metallic oxides, in the same manner, viz., to metallic fluorides and water.

2. The fluorides of the alkali metals are soluble in water, whilst those with the metals of the alkaline earths are either altogether insoluble in water, or dissolve in this menstruum with very great difficulty. Fluoride of aluminum is readily soluble. Most of the fluorides corresponding with the oxides of the heavy metals are very sparingly soluble in water; this is the case, for instance, with fluoride of copper, fluoride of lead, fluoride of zinc; many other fluorides dissolve in water without difficulty, such are, for instance, the perfluoride of iron, protofluoride of tin, perfluoride of mercury, &c. Of those compounds which are either insoluble or but sparingly soluble in water, many dissolve in free hydrofluoric acid, whilst others remain undissolved in this menstruum. Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Chloride of calcium* produces in aqueous solutions of hydrofluoric acid or of fluorides, a gelatinous precipitate of FLUORIDE OF CALCIUM, ($Ca\,Fl$,) which is so transparent, as at first to induce the belief, that the fluid has remained perfectly clear and unaltered. The addition of ammonia promotes the complete separation of the precipitate. The precipitated fluoride of calcium is insoluble in hydrochloric acid and nitric acid, and also in alkaline fluids in the cold; a trace of it dissolves, however, upon

boiling with hydrochloric acid. It is scarcely more soluble in free hydrofluoric acid, than in water.

4. If any finely-levigated fluoride be mixed with pounded *glass* or *sand*, the mixture drenched in a test tube, with *concentrated sulphuric acid*, and heat applied, FLUOSILICIC GAS will be evolved, which will form dense white fumes in moist air. If this gas be transmitted through water—(by means of a bent tube fitted to the test-cylinder)—silicic acid will separate as a gelatinous mass, and hydrofluosilicic acid will be formed, which latter imparts a strongly acid reaction to the fluid. Compare § 46. When operating upon very minute quantities, it is advisable to transmit the gas simply through a glass tube, moistened within, when the evolution of fluosilicic gas will be clearly indicated by the separation of silicic acid, which impairs the transparency of the tube in its whole length.

5. If the solution of a fluoride, mixed with sulphuric acid, be poured over a glass plate, coated with bees-wax, which has here and there been removed again by means of a pointed instrument,* and the fluid be allowed to dry upon the plate, the exposed lines will, upon the subsequent removal of the wax, be found etched into the glass. When operating upon very minute quantities, the mixture of the fluoride with sulphuric acid may be simply poured into a watch-glass, and evaporated to dryness, at a gentle heat, when, upon the subsequent removal of the residue with water, the internal surface of the glass will appear dimmed.

6. If a finely-levigated fluoride, no matter whether soluble or insoluble, be drenched in a platinum crucible with concentrated sulphuric acid, the crucible covered with a glass plate, prepared as directed at 5, and then exposed to a gentle heat

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* The coating of the plate may be readily effected by melting some wax upon it, and allowing the fused mass to spread equally over the surface; the instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers the purpose best. The subsequent removal of the wax is effected by heating the plate, wiping the fused mass off, and washing the plate finally with oil of turpentine.

for the space of from fifteen to thirty minutes, the exposed lines will, upon the subsequent removal of the wax, be found etched into the glass. Care must be taken in this process to prevent the melting of the wax; it is advisable for this purpose to keep the upper surface of the plate moistened with water. If the quantity of hydrofluoric acid disengaged by the sulphuric acid be very minute, the etching will frequently be altogether invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This reappearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess.

Remarks.—The third section embraces phosphoric acid, boracic acid, oxalic acid, and hydrofluoric acid. We have seen that the barytes compounds of these acids are dissolved by hydrochloric acid, apparently without undergoing decomposition; alkalies therefore reprecipitate them unaltered, by neutralizing the hydrochloric acid. The barytes compounds of arsenious acid, arsenic acid, and chromic acid present, however, the same deportment, and must therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from this reprecipitation of a salt of barytes by alkalies. But even leaving this point altogether out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric solutions the salts of barytes in question, and more particularly the borate of barytes, whenever the solution contains any considerable proportion of free acid, or of an ammoniacal salt. Boracic acid may be detected invariably by the characteristic tint which it communicates to the flame of alcohol, provided care be taken to concentrate the solution sufficiently before adding the alcohol, and in the case of borates, to mix the solution with a sufficient amount of sulphuric acid, (concentrated sulphuric acid answers the purpose best). Upon evaporating solutions of free boracic acid, the acid is to be combined with an alkali, since otherwise a large portion of it will volatilize with the aqueous vapors. Phosphoric acid is sufficiently characterized by the yellow precipitate of phosphate of silver, by the characteristic properties of the basic phosphate of magnesia and ammonia, (more particularly the insolubility of this compound in sal ammoniac,) by the deportment of phosphate of lead before the blow-pipe, and finally and more particularly by the reaction with perchloride of iron and acetate of potass; if an excessive amount of perchloride of iron be added, in the latter process, a far less copious precipitate will form, and, in some instances, the reagent will altogether fail to produce a precipitate, since perphosphate of iron is soluble in peracetate of iron.—Oxalic acid may always be readily detected by solution of gypsum; it is only necessary to bear in mind that the precipitated oxalate of lime does not redissolve in acetic acid, (phosphate of lime,) but redissolves readily in dilute hydrochloric acid, and changes upon ignition, to carbonate of lime, differing in this from fluoride of calcium. The oxalates of the alkaline earths are completely decomposed by boiling with carbonate of soda. Hydrofluoric acid, finally, cannot readily be confounded with other acids; the reaction described at *d.* 4. affords, under all circumstances, the most positive test and proof of the presence of this acid. The reactions described at *d.* 5. and 6. are applicable only in the absence of silicic acid; this is to be borne in mind when testing for hydrofluoric acid.

Fourth Section of the First Group of the Inorganic Acids.

§ 100.

a. CARBONIC ACID. ($C\,O_2$.)

1. Carbonic acid at the common temperature and common atmospheric pressure is a colorless gas of far greater specific

gravity than the air, so that it may be poured from one vessel into another. It dissolves in water; the solution has a feebly acid pungent taste; upon applying heat to the solution, the carbonic acid escapes.

2. Part of the carbonates lose their carbonic acid upon ignition. All the carbonates with colorless oxides are white or colorless. Only those with alkaline bases are soluble in water in the neutral state. The solutions manifest a very strong alkaline reaction. The bicarbonates with alkaline bases are soluble in water, and so are also the bicarbonates of the alkaline earths and some of the bicarbonates with metallic bases.

3. The carbonates are decomposed by all free *acids* soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. The decomposition of the carbonates by acids is attended with EFFERVESCENCE, the carbonic acid being disengaged as a colorless and almost inodorous gas which imparts a transient reddish tint to litmus paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkaline bases, since the formation of bicarbonates will frequently prevent effervescence, if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid, by this method, should first be drenched with water to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substance with the test-acid. Should it be desirable to determine by a direct experiment whether the disengaged gas is really carbonic acid or not, this may be readily accomplished by transferring some of the disengaged gas (but none of the fluid) from the test-cylinder into another tube, adding some lime-water to it, and agitating the tube. The formation of a copious precipitate will prove that the evolved gas is really carbonic acid.

4. *Lime-water* and *water of barytes*, when brought into contact with carbonic acid or with soluble carbonates, produce white precipitates of neutral CARBONATE OF LIME, ($Ca\ O,\ C\ O_2$,) or neutral CARBONATE OF BARYTES, ($Ba\ O,\ C\ O_2$). When testing

for free carbonic acid, these reagents ought always to be added in excess, since the acid carbonates of the alkaline earths are soluble in water. The precipitated carbonates of lime and barytes dissolve in acids, with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition.

5. *Chloride of calcium* and *chloride of barium* produce in solutions of neutral alkaline carbonates immediately precipitates of CARBONATE OF LIME or of CARBONATE OF BARYTES; in solutions of bicarbonates these precipitates are formed only upon ebullition; with free carbonic acid these reagents yield no precipitate.

b. SILICIC ACID. ($Si\,O_2$.)

1. Silicic acid occurs in two modifications; the one is soluble in water and acids, the other is affected by hydrofluoric acid alone. The action of heat converts the soluble into the insoluble modification. The fusion of the insoluble modification, with pure alkalies or alkaline carbonates, gives rise to the formation of a basic alkaline silicate, which is soluble in water, and from which acids separate the silicic acid in its soluble modification. The soluble modification dissolves readily when boiled with potass ley or solution of carbonate of potass; the insoluble modification dissolves only very slowly in the same menstrua. The silicates of the alkalies alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids;* when the solutions are highly concentrated, the SILICIC ACID separates in the form of gelatinous flakes, whilst it remains dissolved in more dilute solutions. If a dilute solution of an alkaline silicate be mixed with an acid, (hydrochloric acid or nitric acid,) and the mixture subsequently evaporated to dryness, the silicic acid will be converted from its soluble into its insoluble modification, and will remain as a white gritty powder when the residue is treated with water. The addition of salammoniac to solutions of alkaline silicates also causes precipitation of hydrated silicic acid.

3. In the silicates with earthy or metallic bases, the silicic acid exists also either in its soluble or in its insoluble modification. The silicates with the soluble modification are decomposed by boiling hydrochloric or nitric acid, the silicic acid separating as gelatinous hydrate, whilst the decomposing acid combines with the base. But these acids fail to act upon silicates with the insoluble modification of silicic acid. To effect the separation of the silicic acid from silicates of the latter description, these are to be either treated in the humid way with hydrofluoric acid, or fused with alkaline carbonates.

4. *Carbonate of soda* dissolves a copious amount of silicic acid in the flame of the blow-pipe to colorless buttons of SILICATE OF SODA, which remain transparent on cooling; the carbonic acid escapes with effervescence in this process. Inexperienced students often fail to produce a clear button, because they use too much carbonate of soda in proportion to the quantity of the test-specimen.

5. *Phosphate of soda and ammonia* fails nearly altogether to dissolve silicic acid. The silicic acid floats about in the transparent button as an opaque mass, and may therefore be seen better in the ignited than in the cold button. The silicates show the same deportment; the phosphate of soda and ammonia withdraws their base from them, and separates silicic acid. The bases are generally dissolved, whilst the silicic acid remains undissolved.

Recapitulation and remarks.—Carbonic acid is generally very easily detected by the nearly inodorous gas which is evolved when the carbonates are treated with acids. When operating upon compounds which, besides carbonic acid gas, evolve other gases, the disengaged gas is to be tested with lime water or with water of barytes. Silicic acid in its soluble modification, (into which it must invariably be converted,) may be positively detected, under all circumstances, by supersaturating its compounds with hydrochloric acid, evaporating to dryness, treating the residue with water, and testing the undissolved part before the blow-pipe.

Second Group of the Inorganic Acids.

ACIDS WHICH ARE PRECIPITATED BY NITRATE OF SILVER, BUT NOT BY CHLORIDE OF BARIUM: *Hydrochloric Acid—Hydrobromic Acid—Hydriodic Acid—Hydrocyanic Acid—Hydrosulphuric Acid.*

§ 101.

All the silver compounds of the acids belonging to this group are insoluble in dilute nitric acid. The acids of this group transpose with metallic oxides; the metals combine with the chlorine, bromine, cyanogen, iodine, or sulphur, whilst the oxygen of the metallic oxides forms water with the hydrogen of the hydracids.

a. HYDROCHLORIC ACID. ($Cl\,H.$)

1. Hydrochloric acid, at the common temperature and common atmospheric pressure, is a colorless gas which forms dense fumes in the air, is suffocating and very irritant, and dissolves in water with exceeding facility. The solution (common hydrochloric acid) loses a large portion of the hydrochloric gas upon heating.

2. The neutral chlorides are readily soluble in water, with the exception of chloride of lead, chloride of silver, and protochloride of mercury; most of the chlorides are colorless. Many of them volatilize at a high temperature, without suffering decomposition; many of the chlorides decompose upon ignition, and but few of them are fixed.

3. *Nitrate of silver* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides, white precipitates of CHLORIDE OF SILVER, ($Ag\,Cl$,) which, when exposed to light, turn first violet, and subsequently black, are insoluble in nitric acid, but dissolve readily in ammonia, and fuse without decomposition, when heated. (Vide § 91. *a.* 5.)

4. *Protonitrate of mercury* and *acetate of lead* produce in solutions containing free hydrochloric acid or chlorides, precipitates of PROTOCHLORIDE OF MERCURY (Hg_2 Cl) and CHLORIDE OF LEAD (Pb Cl.) For the properties of these precipitates, vide § 91. *b*. 5, and *c*. 6.

5. When chlorides are heated in with *peroxide of manganese* and *sulphuric acid*, chlorine is evolved, which may be readily recognized by its odor and YELLOWISH-GREEN color.

6. If a triturated mixture of a chloride with *chromate of potash*, be treated with *concentrated sulphuric acid*, in a tubular retort, at a gentle heat, a deep brownish-red gas will be copiously evolved; (CHROMATE OF PERCHLORIDE OF CHROMIUM, $Cr\ Cl_3 + 2\ Cr\ O_3$;) this gas condenses into a fluid of the same color, and passes over into the receiver. If this chromate of perchloride of chromium is mixed with ammonia in excess, a yellow-colored liquid is produced; the yellow tint is imparted to the fluid by the chromate of ammonia which forms in this process; upon the addition of an acid, the yellow color of the solution changes to a reddish-yellow, owing to the formation of acid chromate of ammonia.

b. HYDROBROMIC ACID. (Br H.)

1. Hydrobromic acid gas, its aqueous solution, and the metallic bromides, offer in their general deportment a great analogy with the corresponding chlorides.

2. *Nitrate of silver* produces in aqueous solutions of hydrobromic acid and bromides a yellowish-white precipitate of BROMIDE OF SILVER, (Ag Br,) which changes to violet upon exposure to the light; this precipitate is insoluble in dilute nitric acid, and somewhat sparingly soluble in ammonia.

3. *Nitric acid* decomposes hydrobromic acid and the bromides, —(with the exception of bromide of silver and perbromide of mercury,)—upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal. The liberated bromine colors the solution yellowish-red. When operating upon

bromides in the solid state, yellowish-red vapors of bromine gas escape, emitting the odor of chlorine; these vapors, when evolved in sufficient quantity, condense in the cold part of the test-tube into small drops.

4. *Chlorine gas,* or *solution of chlorine,* liberates bromine also in the solutions of its compounds; the fluid assuming a yellowish-red tint, if the quantity of the bromine present is not too minute. If a yellow-colored solution of this kind be agitated with some *ether,* it will lose its color, the whole of the bromine present dissolving in the ether, which will now appear distinctly yellow, even though but a very minute quantity of bromine be present. If the ethereal solution of bromine be now agitated with some potass ley, the yellow tint will again disappear, and the solution will now contain bromide of potassium and bromate of potass. Upon the evaporation of this solution, and subsequent ignition of the residue, the bromate of potass is converted into bromide of potassium, and this may then be further tested as directed at 5.

5. If bromides are heated with *peroxide of manganese* and *sulphuric acid,* YELLOWISH-RED VAPORS OF BROMINE are evolved. If the bromine is present only in very minute quantity, the color of these vapors may not be visible. The experiment is, in that case, to be conducted in a small retort, and the evolved vapors are to be transmitted through a long condensing glass tube, and finally received into small test-cylinders, containing some moistened starch.

6. When moist *starch* is brought into contact with free bromine, no matter whether in solution or in the gaseous state, YELLOW BROMIDE OF STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by closing the test-tube which contains the starch drenched with the fluid under examination, before the blow-pipe, and subsequently inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine will now impart a

yellow tint to the starch, after the lapse of from 12 to 24 hours. This tint will finally disappear again after the lapse of some time.

7. If a mixture of a bromide with *chromate of potash* be drenched with sulphuric acid, and heat applied, a brownish-red gas will be evolved, in the same manner as is the case with the chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over, will not turn yellow, but colorless, upon supersaturation with ammonia.

c. HYDRIODIC ACID. ($I\,H$.)

1. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gas, it dissolves copiously in water. The colorless hydrated hydriodic acid turns speedily to a reddish-brown when in contact with the air; this is owing to the formation of hydriodous acid ($I_2\,H$) and water.

2. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, far more are insoluble in water than is the case with the corresponding chlorides. Many iodides show characteristic colorations.

3. Nitrate of silver produces in aqueous solutions of hydriodic acid and of IODIDES, yellowish white precipitates of IODIDE OF SILVER, ($Ag\,I$,) which turn black when exposed to the light; these precipitates are insoluble in dilute nitric acid, and but very sparingly soluble in ammonia.

4. A solution of one part of *sulphate of copper*, and two and a quarter parts of *protosulphate of iron*, throws down from aqueous neutral solutions of the iodides, PROTIODIDE OF COPPER, ($Cu_2\,I$) in the form of a dirty-white precipitate. The addititiion of some ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent, (sulphate of copper and protosulphate of iron.)

5. *Nitric acid* decomposes the hydriodic acid and the iodides in the same manner as the corresponding bromides. Colorless solutions of hydriodic acid or of the iodides acquire therefore

immediately a brownish-yellow tint upon the addition of nitric acid, even in the cold; and from concentrated solutions the IODINE separates as a black precipitate, whilst nitric oxide gas escapes with effervescence. Solid iodides, when heated with nitric acid, evolve, besides nitric oxide gas, VIOLET vapors of iodine, which condense upon the colder parts of the vessel into a blackish sublimate.

6. *Chlorine gas,* and *solution of chlorine,* liberate iodine likewise from the iodides, but the liberated iodine combines with these reagents when added in excess, to colorless CHLORIDE OF IODINE.

7. If iodides are heated with concentrated *sulphuric acid,* or with *sulphuric acid* and *peroxide of manganese,* IODINE is liberated, which may be readily recognized by the violet color of its vapor. If concentrated sulphuric acid alone be used, sulphurous acid will be evolved in conjunction with the iodine. Should the quantity of iodine present be very minute, the characteristic color of its vapor will not appear distinctly, and the operator will be obliged to resort to the use of starch; viz.

8. If to a solution of iodine or of hydriodic acid, or of an iodide—(in which latter case, the iodine is to be liberated first by addition of nitric acid)—thin *starch paste* be added, the fluid will acquire a more or less violet or blackish-blue tint, owing to the formation of IODIDE OF STARCH, even though only the most minute traces of iodine be present. Should the amount of iodine present be considerable, a blackish-blue precipitate of iodide of starch will be formed. If solutions of chlorine be used to effect the liberation of the iodine, this should be added very cautiously to prevent the formation of chloride of iodine, since no blue solution would appear in that case, chloride of iodine being a colorless substance. The best way of detecting the iodine in dry compounds of any description is, to introduce the compound under examination into a flask, to pour concentrated sulphuric acid over it, and to close the flask loosely with a stopper to which is attached a moistened slip of paper, or better still, white cotton

cloth, covered with starch powder, or imbued with starch paste. After the lapse of a few hours this will acquire a blue tint, even though only a minute trace of iodine be present.

9. The iodides manifest with sulphuric acid in conjunction with chromate of potass (compare § 101. *a.* 6.) the same deportment they exhibit with sulphuric acid alone.

d. HYDROCYANIC ACID. (Cy H.)

1. Hydrocyanic acid is a colorless, volatile, inflammable liquid, the odor of which resembles that of bitter almonds; it is miscible with water in all proportions, and speedily undergoes spontaneous decomposition when in its pure state.

2. Those cyanides which have an alkali or alkaline earth for base, are soluble in water as hydrocyanates. They are readily decomposed by acids, even by carbonic acid, but ignition fails to decompose them when the access of air is precluded. When fused with oxides of lead, copper, antimony, tin, &c., the cyanides reduce these oxides, and are converted into cyanates. Only a few of those cyanides which contain heavy metals are soluble in water; all of them are decomposed upon ignition, and resolved either into cyanogen gas, and metal, such are the cyanides of the noble metals, or into nitrogen gas and carburets; such are the cyanides of the other heavy metals. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and but with difficulty by concentrated nitric acid. Hydrochloric acid and sulphuretted hydrogen decompose most of them readily and completely.—Cyanogen combines with several metals, (iron, manganese, cobalt, chromium,) forming compound radicals, in which many of the usual methods will fail to detect the presence of the metals.

3. *Nitrate of silver* produces, in solutions of free hydrocyanic acid and of alkaline hydrocyanates, white precipitates of CYANIDE OF SILVER, (Ag Cy) which are readily soluble in cyanide of potassium, dissolve with some difficulty in ammonia, and are

insoluble in nitric acid; these precipitates are decomposed upon ignition, and leave metallic silver with some paracyanide of silver.

4. The addition of a solution of *protosulphate of iron* which has been for some time in contact with the air, to the solution of an alkaline hydrocyanate, gives rise to the formation of ferrocyanide of potassium, which remains in solution, and, if free alkali is present, of hydrated ferroso-ferric oxide, which precipitates. If hydrochloric acid be now added in excess, this precipitate will redissolve, and a new precipitate of PRUSSIAN BLUE will be formed, or the fluid will at least acquire a blue tint. (Compare § 89. *f.* 6.) Free hydrocyanic acid must consequently first be combined with an alkali before its detection by this method can be attempted.

5. If to a solution of hydrocyanic acid, potass be added in excess, and subsequently finely levigated *peroxide of mercury*, the latter substance will readily dissolve exactly as it would in free hydrocyanic acid. Since peroxide of mercury is soluble in alkaline fluids *only in presence of hydrocyanic acid*, this reaction may be looked upon as a positive test for hydrocyanic acid.

6. Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. The following process is pursued to detect the radical in this compound. The solution under examination is mixed with hydrochloric acid and metallic iron. This gives rise to the separation of metallic mercury, and formation of hydrocyanic acid and protochloride of iron, (which latter changes partially to perchloride in the air). If potass be now added to the fluid, ferrocyanide of potassium and ferroso-ferric oxide will be formed, and finally, upon subsequent supersaturation with hydrochloric acid, Prussian blue. Cyanide of mercury may be readily decomposed also by sulphuretted hydrogen, with which it transposes into the sulphurets of mercury and hydrocyanic acid. The action of heat, as already stated at 2. resolves the cyanide of mercury into metallic mercury and cyanogen gas, which latter may be readily recognized by

the characteristic effect which it produces upon the olfactory organs, and moreover by the crimson tint of its flame.

7 In the ferro and ferri-cyanides with alkaline bases, the ferro and ferri-cyanogen may be readily detected, the former by means of *solution of a persalt of iron,* or *solution of a proto-salt of copper,* and the latter by means of solution of *proto-salt of iron.* The distillation of these double cyanides with sulphuric acid gives rise to the evolution of free hydrocyanic acid. The insoluble ferrocyanides and ferricyanides undergo decomposition, when heated with caustic potass, or with carbonate of potass; ferrocyanide of potassium is formed, and the metals separate as pure oxides, or as carbonates.

e. HYDROSULPHURIC ACID. (H S.)

Sulphuretted Hydrogen Gas.

1. Sulphuretted hydrogen, at the common temperature and under common atmospheric pressure, is a colorless, inflammable gas, soluble in water, and which may be readily recognized by its characteristic smell of rotten eggs.

2. The sulphurets with alkaline, or alkaline earthy bases are alone, soluble in water. These, and the sulphurets of metals of the fourth group, such as the sulphurets of iron and manganese for instance, are decomposed by dilute mineral acids, with evolution of sulphuretted hydrogen gas, which may be readily detected by its peculiar smell, and by its action upon solution of lead. (Vide 3.) The decomposition of higher sulphurets is attended also with separation of sulphur in a highly divided state; this sulphur precipitate may be readily distinguished from similar precipitates by its inflammability. Part of the sulphurets of the fifth and sixth group are decomposed by concentrated and boiling hydrochloric acid, with evolution of sulphuretted hydrogen gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury resist the action of both

hydrochloric and nitric acids, but dissolve readily in aqua regia. Upon the solution of sulphurets in nitric acid, and in aqua regia, sulphuric acid is formed, and the process of solution is, moreover, attended with separation of sulphur in most cases, which is readily recognized by its color and by its deportment upon heating.

3. When sulphuretted hydrogen in solution, or in the gaseous form, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates of SULPHURET OF SILVER or SULPHURET OF LEAD are formed. (Vide § 91. *a.* and § 91. *c.*) In cases, therefore, where the mere smell fails to afford sufficient proof of the presence of sulphuretted hydrogen, this reagent will lead to positive conviction. When the sulphuretted hydrogen is present in the gaseous form, a small slip of paper, moistened with solution of basic acetate of lead, is to be placed in the air which it is intended to test for the presence of this gas; if sulphuretted hydrogen be present, this paper will become covered with a thin, brownish-black and lustrous film of sulphuret of lead.

4. When sulphurets are exposed to the *oxidizing flame of the blow-pipe,* the sulphur burns with a blue flame, emitting at the same time the well-known odor of sulphurous acid.

Recapitulation and remarks.—Most of the acids of the first group are likewise precipitated by nitrate of silver, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are *soluble* in dilute nitric acid, whilst the latter are *insoluble* in that menstruum. The presence of hydrosulphuric acid interferes more or less with the testing for the other acids of the second group; this acid must, therefore, if present, be removed first, before we can proceed to test for the other acids. The removal of the hydrosulphuric acid, when present in the free state, may be effected by simple ebullition, and when present in the form of an alkaline sulphuret by the addition of a metallic salt, such as will not precipitate any of the other acids, or at least will not precipitate them from acid solutions. Hydriodic and hydrocyanic acid may be detected even in presence of hydrochloric or hydrobromic acid, by the equally characteristic and delicate reactions with starch and with solution of ferroso-ferric oxide. But the detection of chlorine and bromine is more or less difficult in presence of iodine and cyanogen. Should these latter substances be present, it will be necessary therefore to remove them before proceeding to test for chlorine and bromine. The separation of the cyanogen may be readily effected by converting the whole of the radicals present into salts of silver, and igniting subsequently the mixed compound produced, when the cyanide of silver will undergo decomposition, whilst the chloride, bromide, and iodide of silver will remain unaltered. The iodine may now be separated from the chlorine and bromine, by treating the mixed silver compound with ammonia, since the iodide of silver is nearly altogether insoluble in that menstruum. A still more accurate separation may be effected by precipitating the iodine as protiodide of copper, since the whole of the chlorine and bromine remains in solution in this process. Bromine is to be detected by the side of chlorine, by adding to the mixed compound under examination, solution of chlorine, or hydrochloric acid and chloride of lime, and dissolving the liberated bromine subsequently with ether. Chlorine by the side of bromine may be detected by the reaction which it manifests with chromate of potass and sulphuric acid.

Third Group of the inorganic Acids.

ACIDS WHICH ARE NOT PRECIPITATED BY SALTS OF BARYTES NOR BY SALTS OF SILVER: *Nitric Acid—Chloric Acid.*

§ 102.

a. NITRIC ACID. (NO_5.)

1. Nitric acid cannot be exhibited in the anhydrous state. The hydrate of pure nitric acid is a colorless, exceedingly caustic fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors nitrogenous mat-

ter intensely yellow. Admixture of nitrous acid imparts to hydrated nitric acid a red color.

2. All the neutral salts of nitric acid are soluble in water; only a few of the basic nitrates are insoluble in this menstruum. All nitrates without exception undergo decomposition at an intense red heat. Those with alkaline bases yield oxygen and nitrogen; the rest yield oxygen and nitrous or hyponitric acid.

3. When a nitrate is thrown upon *red-hot charcoal,* or when charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion, DEFLAGRATION takes place, i. e. the charcoal burns at the expense of the oxygen of the nitric acid, the combustion being attended with vivid scintillation.

4. If the mixture of a nitrate with *cyanide of potassium* in powder be heated on a platinum plate, a vivid DEFLAGRATION will ensue, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

5. If the solution of a nitrate be mixed with one-fourth part of its quantity of concentrated sulphuric acid, and a chrystal of *protosulphate of iron* thrown into the refrigerated mixture, the fluid immediately surrounding this chrystal will acquire a DARK BROWN TINT. This coloration will disappear again generally upon simple agitation of the fluid, and invariably upon the application of heat. In this process, the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combines with the protoxide, and converts a portion of it into peroxide, and the remaining nitric oxide combines with the remaining portion of the protoxide of iron, forming a peculiar soluble compound, which, upon its solution in the water of the menstruum, imparts a brownish-black color to the latter.

6. If to the solution of a nitrate some sulphuric acid be added, and as much *solution of indigo* in sulphuric acid as will impart a faint light-blue tint to the fluid, and the mixture be heated to boiling, the blue coloration of the fluid will change to a faint yellowish tint, or the solution will even become perfectly colorless. This change of color is owing to the oxidation of the indigo at

the expense of the oxygen of the nitric acid which is liberated by the sulphuric acid. It must be borne in mind, however, that several other substances besides nitric acid, cause decoloration of solution of indigo—free chlorine particularly produces this effect.

7. If concentrated sulphuric acid be poured over the mixture of a nitrate with *copper-filings*, in a test-tube, the air in the latter will acquire a yellowish-red tint, owing to the nitric oxide gas which is liberated upon the oxidation of the copper by the nitric acid combining with the oxygen of the air and forming nitrous acid. This coloration may be observed most distinctly by looking through the tube in the direction of its length.

b. CHLORIC ACID. ($Cl\,O_5$.)

1. Chloric acid forms in its most highly concentrated solution a yellow oily fluid the odor of which resembles that of nitric acid. It reddens litmus first and bleaches it subsequently. Dilute chloric acid is colorless and inodorous.

2. All chlorates are soluble in water. When chlorates are heated to redness, the whole of their oxygen escapes and metallic chlorides remain.

3. When heated with *charcoal* or some organic substance, the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. When the mixture of a chlorate with *cyanide of potassium* is heated on a platinum plate, DEFLAGRATION takes place, attended with strong detonation and ignition, even though the chlorate be present only in very minute quantity. (This experiment should be made with minute quantities only.)

5. Free chloric acid oxidizes and decolors *indigo* in the same manner as nitric acid; consequently if the solution of a chlorate be mixed with sulphuric acid and solution of indigo, and the mixture be heated to boiling, the same phenomena will manifest themselves which we have described while treating of nitric acid, (vide *a.* 6).

6. If the solution of a chlorate be colored light blue with a

small amount of *solution of indigo* in sulphuric acid, and a solution of *sulphurous acid* in water be subsequently dropped cautiously into the blue fluid, the color of the indigo will disappear. The cause of this equally characteristic and delicate reaction is this: the sulphurous acid deprives the chloric acid of its oxygen and the thus liberated chlorine decolors the indigo.

7. Upon heating chlorates with *hydrochloric acid,* the constituents of the two acids transpose into water and bichlorate of chlorous acid ($2\ Cl\ O_5 + Cl\ O_3$).

8. *Concentrated sulphuric acid,* when poured over a chlorate, causes the conversion two-thirds of the metallic oxide into a sulphate and the remaining one-third into a hyperchlorate; this conversion is attended, moreover, with liberation of chlorate of chlorous acid, which imparts an intensely yellow tint to the sulphuric acid, and manifests its presence, moreover, by its odor and the greenish color of the evolved gas. [$3\ (KO, Cl\ O_5) + 4\ SO_3 = 2\ (KO, 2\ SO_3) + KO, Cl\ O_7) + (Cl\ O_5 + Cl\ O_3)$]. The application of heat must be avoided in this experiment, and the quantities operated upon, should be very minute, since otherwise the decomposition might ensue with such force and energy as to cause an explosion.

Recapitulation and remarks.—Of all the reactions which have been suggested to effect the detection of nitric acid, those with proto-sulphate of iron and sulphuric acid, and with copper filings and sulphuric acid, yield the most positive results; with regard to deflagration with charcoal, detonation with cyanide of potassium, and decoloration of solution of indigo, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only when no chloric acid is present. The best way to ascertain whether chloric acid be present or not, is to ignite the sample under examination, to dissolve the mass subsequently, and to test the solution finally with nitrate of silver. Should a chlorate be present, this will be converted into a chloride upon the ignition of the sample, and nitrate of silver will now precipitate chloride of silver from the solution of the sample. However, this test is thus simple only when no chloride happens to be present with the chlorate. But should the substance under examination contain an admixture of chloride, it will be necessary, in the first place, to add nitrate of silver to its solution, until this ceases to produce a precipitate; the fluid is then to be filtered off from the latter, and the filtrate subsequently evaporated and the residue ignited. It is, however, generally unnecessary to pursue this circuitous way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid.

II. ORGANIC ACIDS.

First Group.

ACIDS WHICH ARE PRECIPITATED BY CHLORIDE OF CALCIUM, UNDER CERTAIN CONDITIONS: *Oxalic Acid—Tartaric Acid—Paratartaric or Racemic Acid—Citric Acid—Malic Acid.*

§ 103.

None of these acids volatilize without suffering decomposition.

a. OXALIC ACID.

For the reactions of oxalic acid I refer to § 99. *c.*

b. TARTARIC ACID. ($C_4\,H_2\,O_5 = T.$)

1. Tartaric acid forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in spirit of wine. Tartaric acid when heated fuses at first, and becomes subsequently carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar.

2. The tartrates with alkaline bases are soluble in water, and so are those with the metallic oxides of the third and fourth

group; those of the tartrates which are insoluble in water, dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness; charcoal separates and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of a tartrate, solution of *peroxide of iron,* or of *protoxide of manganese* or of *alumina* be added, and subsequently ammonia or potass, no precipitation of peroxide of iron, or of protoxide of manganese or of alumina will ensue, since the new-formed double tartrates are not decomposed by alkalies. Tartaric acid prevents likewise the precipitation of several other oxides by alkalies.

4. Free tartaric acid yields with *salts of potass,* and more particularly with acetate of potass, a sparingly soluble precipitate of BITARTRATE OF POTASS. The same precipitate is formed, when acetate of potass and free acetic acid, or bisulphate of potass, are added to the solution of a neutral tartrate. When using bisulphate of potass, addition in excess is to be most carefully avoided. The acid tartrate of potass dissolves readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The precipitation of the bitartrate of potass may be greatly promoted by violent agitation.

5. *Chloride of calcium* throws down from the solutions of neutral tartrates, white precipitates of TARTRATE OF LIME ($CaO, \bar{T}$.) Presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid, or friction on the sides of the vessel, promotes the separation of the precipitate. Tartrate of lime dissolves in a cold solution of caustic potass to a clear fluid. But upon boiling this solution, the dissolved tartrate of lime separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* produces in solutions of neutral tartrates, or even in solutions of free tartaric acid, (if added till an alkaline reaction becomes manifest,) white precipitates which dissolve

readily in tartaric acid, and also in solution of sal ammoniac; after the lapse of several hours, the tartrate of lime separates again from the solutions in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of gypsum* fails to produce a precipitate in a solution of tartaric acid; in solutions of neutral tartrates, this reagent produces a minute precipitate, after the lapse of some time.

c. PARATARTARIC ACID. (RACEMIC ACID.) ($C_4 H_2 O_5 = \overline{R}$.)

1. Racemic acid has the same composition as tartaric acid. In its crystallized state it contains two equivalents of water, of which it loses one at 212°. It effloresces very slowly in dry air. Its deportment with solvents, and when acted upon by heat, is analogous to that which tartaric acid exhibits under the same circumstances.

2. The deportment and properties of the paratartrates are very similar to those of the corresponding tartrates. Many of the paratartrates differ, however, from corresponding tartrates, in form, solubility, and proportional amount of water. The paratartrates prevent, like the tartrates, the precipitation of alumina, protoxide of manganese, peroxide of iron, &c., by alkalies.

3. *Chloride of calcium* precipitates both from the solutions of free paratartaric acid of paratartrates, PARATARTRATE OF LIME, ($Ca O, \overline{R}$), as a dazzling white powder. This precipitate is insoluble in sal ammoniac, but it dissolves completely in cold concentrated potass ley, and partially in dilute solution of potass; this solution turns turbid and gelatinous upon boiling, and clears again upon cooling.

4. *Lime-water* produces in solutions of neutral paratartrates, instantaneously, white precipitates of PARATARTRATE OF LIME. It produces the same precipitate in solution of free paratartaric acid, if added to alkaline reaction; but if a less amount of lime-water be used, so as to leave the solution still acid, the precipitate will form only after the lapse of a few moments. Paratartrate of lime is insoluble both in paratartaric and tartaric

acid ; it dissolves in hydrochloric acid, and precipitates again from this solution instantaneously, or after a few moments, upon addition of ammonia in excess.

5. *Solution of gypsum* produces immediately in solutions of neutral paratartrates a precipitate of paratartrate of lime ; but from solutions of free paratartaric acid, this precipitate separates only after the lapse of from ten to fifteen minutes.

6. If crystallized paratartaric acid, or a paratartrate be heated with *concentrated sulphuric acid,* the latter will acquire a black color, and sulphurous acid and carbonic oxide gas will be evolved. Tartaric acid presents the same deportment.

d. CITRIC ACID. ($C_4 H_2 O_4 = \overline{Ci}$.)

1. Citric acid crystallizes in colorless, pellucid, and inodorous crystals of an agreeable acid taste, and which, according to the circumstances attendant upon its formation, contain, besides one equivalent of hydration water, varying amounts of crystallization water. Citric acid is unalterable in the air, and dissolves readily in water and in alcohol. When subjected to the action of heat, citric acid fuses at first, and carbonizes subsequently, with emission of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization.

2. The citrates with alkaline bases are readily soluble in water, both in the neutral and acid state ; the same applies to the compounds of citric acid with such of the metallic oxides as are weak bases, with peroxide of iron, for instance. Citrates prevent, like tartrates, and for the same reason, the precipitation of peroxide of iron, protoxide of manganese, alumina, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solution of free citric acid, even upon boiling ; but a precipitate of NEUTRAL CITRATE OF LIME ($Ca O, \overline{Ci}$) will immediately form if the free citric acid be saturated with potass or soda. This precipitate is in-

soluble in potass, but it dissolves readily in solution of sal ammoniac; upon boiling this solution, neutral citrate of lime separates again in the form of a white crystalline precipitate. If a solution of citric acid, containing an admixture of chloride of calcium, be saturated with ammonia, no precipitation will ensue in the cold, but upon boiling the clear fluid, neutral citrate of lime will suddenly precipitate.

4. *Lime-water* produces no precipitate in cold solutions of citric acid or of citrates. But upon heating the solution to boiling, with a tolerable excess of hot lime-water, a white precipitate of CITRATE OF LIME is formed, of which the greater portion redissolves upon cooling, simply because it is less soluble in hot than in cold water.

5. *Acetate of lead*, when added in excess, produces in solutions of citric acid, a white precipitate of CITRATE OF LEAD, ($PbO, \bar{Ci}$,) which is very sparingly soluble in ammonia, but dissolves readily in citrate of ammonia. The addition of citric acid in excess to solution of neutral acetate of lead gives equally rise to the formation of a precipitate of citrate of lead; but this precipitate redissolves readily upon the addition of ammonia. We have just now seen that the citrate of lead is but very sparingly soluble in ammonia; the solution therefore is not caused here by the ammonia, but by the citrate of ammonia, which the excess of the acid forms with the ammonia added.

6. Upon subjecting citric acid or citrates with concentrated sulphuric acid to the action of heat, carbonic oxide and carbonic acid escape at first, the sulphuric acid retaining its natural appearance; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

e. MALIC ACID. ($C_4 H_2 O_4 = \bar{M}$.)

1. The composition of malic acid is the same as that of citric acid. It crystallizes with difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Malic acid, when exposed to the action of a heat

of 392°, is resolved into MALEIC ACID, (C_4 H O_3), and FUMARIC ACID (C_4 H O_3). This deportment of malic acid is highly characteristic. When the experiment is made in a small spoon, pungent acid vapors of maleic acid are evolved with effervescence. If the experiment be conducted in a small tube, these fumes will recondense to crystals in the colder part of the tube. The fumaric acid remains as a residue.

2. Malic acid forms with most bases, salts which are soluble in water. The acid malate of potass dissolves in water. Malic acid prevents, like tartaric acid, the precipitation of peroxide of iron by alkalies.

3. *Chloride of calcium* fails to produce a precipitate both in solutions of free malic acid, and of malates. But if, after the addition of the chloride of calcium, alcohol be added to the solution of a malate, MALATE OF LIME (Ca O, $\bar{M}$) will immediately separate in the form of a white powder.

4. *Lime-water* produces no precipitate, either in solutions of free malic acid, or in solutions of malates.

5. *Acetate of lead* throws down from solutions of malic acid and of malates, a white precipitate of MALATE OF LEAD (Pb O, $\bar{M}$). The most distinguishing mark of this precipitate is the lowness of its fusing point; it melts at a temperature below the boiling point of water, and fuses accordingly when the fluid wherein it is suspended is heated to ebullition; the fused mass resembles resin which has been melted under water. This reaction is distinctly marked only when the malate of lead is tolerably pure; admixture of other salts of lead impairs it, or even prevents it altogether.

6. Upon subjecting malic acid, with concentrated sulphuric acid, to the action of heat, the sulphuric acid acquires a black color, and sulphurous acid is evolved.

Recapitulation and remarks.—Of the organic acids of this group, the tartaric acid and paratartaric acid are sufficiently characterized by the sparing solubility of their acid potass salts, by the deportment of their lime salts with potass ley, and by the peculiar odor which they emit upon carbonization. Tartrate of lime is soluble both in free tartaric acid and sal ammonia; whilst the paratartrate of lime is insoluble in these substances. This different deportment of the respective lime salts of the two acids, affords an excellent means to distinguish the latter from one another.—(It must be borne in mind, here, that tartrate of lime separates again from its solution in sal ammoniac, after a shorter or longer space of time, according to the greater or less degree of concentration of the solution.)—Paratartaric acid differs from tartaric acid, moreover, in its deportment with solution of gypsum. The behaviour of paratartaric acid with solution of gypsum, is similar to that which oxalic acid manifests with this reagent. When operating upon the free acids, however, this similarity of deportment is not very liable to occasion mistakes, since the precipitate which solution of gypsum produces in solutions of paratartaric acid, never separates instantaneously. The oxalates, moreover, are to be readily distinguished from the paratartrates by the deportment which they present when exposed to the action of heat by themselves, as well as with sulphuric acid.

Citric acid is recognized most safely and positively by its behaviour with lime water, or with chloride of calcium and ammonia; the sparing solubility of the washed citrate of lead in ammonia, distinguishes citric acid from tartaric and paratartaric acids. The other reagents which produce precipitates or other alterations in the solutions of citric acid and citrates, such as perchloride of gold, and the salts of silver and mercury, &c., present the same or a similar deportment with tartaric and paratartaric acid, and therefore, will not enable us to distinguish between these acids. Malic acid would be sufficiently characterized by the fusion of malate of lead upon ebullition with water, were this reaction more delicate, and not so readily impaired or prevented by the presence of other acids. The formation of a precipitate upon the addition of alcohol to the mixture of a supposed solution

solution of free malic acid, or a malate with chloride of calcium, is to be looked upon as an indication of the presence of malic acid only when the absence of all other acids of which the lime salts are sparingly soluble in water, and altogether insoluble in alcohol, (e. g. sulphuric acid, boracic acid,) is most clearly demonstrated. *At all events, the precipitate produced upon the addition of alcohol, must be subjected to further examination before it can be properly pronounced to consist of malate of lime.* The most positive results are attained by heating the pure malic acid in a glass tube; but this test is not very readily applicable under all circumstances.

Second Group of the Organic Acids.

ACIDS, WHICH CHLORIDE OF CALCIUM FAILS TO PRECIPITATE UNDER ANY CIRCUMSTANCES, BUT WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY PERCHLORIDE OF IRON: *Succinic acid—Benzoic acid.*

§ 104.

a. SUCCINIC ACID. ($C_4 H_2 O_3 = \bar{S}$.)

1. Succinic acid forms colorless and inodorous crystalline scales or prisms, of feebly acid taste, and which are soluble in water, alcohol, and ether, and volatilize without residue when exposed to the action of heat. The officinal acid has an empyreumatic odor, and leaves a small carbonaceous residue, upon volatilization.

2. The succinates are decomposed at a red heat, with the exception of succinate of ammonia; those which have an alkali or alkaline earth for base, are converted into carbonates in this process. Most of the succinates are soluble in water.

3. *Perchloride of iron* produces in solutions of neutral succinates of the alkalies brownish pale red, bulky precipitates of PERSUCCINATE OF IRON ($Fe_2 O_3, \bar{S}_2$). Persuccinate of iron dissolves readily in acids; it is decomposed by ammonia in this manner, that a less bulky precipitate of a highly basic persuccinate of iron separates,

whilst the greater portion of the succinic acid dissolves as succinate of ammonia.

4. *Acetate of lead* yields with succinic acid a white precipitate of neutral SUCCINATE OF LEAD ($Pb\,O, \bar{S}$) which is soluble in an excess of succinic acid, in solution of acetate of lead in nitric acid, also, although less readily, in acetic acid. When acted upon by ammonia the neutral succinate of lead is converted into a basic salt ($3\,Pb\,O, \bar{S}$.)

5. A mixture of *alcohol*, *ammonia*, and *solution of chloride of barium*, produces in solutions of free succinic acid and of succinates, white precipitates of SUCCINATE OF BARYTES ($Ba\,O, \bar{S}$).

6. *Pernitrate of mercury* and *nitrate of silver* also precipitate the succinates; the precipitates, however, are not possessed of any characteristic properties.

b. BENZOIC ACID. ($C_{14}\,H_5\,O_3 = Bz\,O$.)

1. Pure benzoic acid appears in the form of white scales or needles, or simply as a crystalline powder. It volatilizes completely when heated. The fumes of benzoic acid cause a peculiar irritating sensation in the throat, and provoke coughing. The common officinal benzoic acid has the odor of benzoin, and leaves a small carbonaceous residue upon volatilization. Benzoic acid is very sparingly soluble in cold water, but it dissolves pretty readily in hot water, and in alcohol.

2. Most of the benzoates are soluble in water; only those with weak bases, such as peroxide of iron, for instance, are insoluble. The soluble benzoates have a peculiar irritating taste. The addition of a *strong acid* to aqueous solutions of benzoates causes the expulsion of the benzoic acid, which separates in the form of a dazzling white, sparingly soluble powder. Benzoic acid is likewise expelled from the insoluble benzoates by strong acids, which form soluble salts with the bases with which the benzoic acid is comined.

3. Benzoic acid comports itself with *perchloride of iron* like succinic acid. The PERBENZOATE OF IRON, ($Fe_2\,O_3$, $3\,Bz\,O$,)

however, is of a far lighter and more yellowish color than the persuccinate. It is decomposed by ammonia in the same manner as the latter.

4. *Acetate of lead* fails to precipitate free benzoic acid, and likewise benzoate of ammonia, at least immediately; but it produces white flocculent precipitates in solutions of benzoates with fixed alkaline bases.

5. A mixture of *alcohol, ammonia,* and *solution of chloride of barium* produces NO precipitate in solution of free benzoic acid, nor in solutions of the alkaline benzoates.

Recapitulation and remarks.—Succinic and benzoic acid are distinguished from all other acids by their ready volatility and their deportment with perchloride of iron. They differ from one another in the color of their persalts of iron, but principally in their respective degrees of solubility, succinic acid being readily soluble, whilst benzoic acid is very difficult of solution; they differ, moreover, in their respective deportments with chloride of barium and alcohol. Succinic acid is seldom perfectly pure, and may therefore be detected also by the odor of oil of amber which it emits.

The following method will serve to effect the respective detection of benzoic and succinic acid when present side by side: the solution of the compound under examination is precipitated with perchloride of iron, the precipitate formed is heated with ammonia, and the solution thus obtained subsequently filtered. The filtrate is then concentrated by evaporation, and one portion of it finally mixed with hydrochloric acid, another portion with chloride of barium and alcohol.

Third Group of the Organic Acids.

ACIDS WHICH ARE NOT PRECIPITATED, UNDER ANY CONDITION, BY CHLORIDE OF CALCIUM NOR BY PERCHLORIDE OF IRON: *Acetic acid—Formic acid.*

§ 105.

a. ACETIC ACID. ($C_4 H_3 O_3 = \bar{A}$.)

1. The hydrate of acetic acid forms transparent crystalline scales which fuse at 63° to a colorless fluid of a peculiar pungent odor and exceedingly acid taste. When exposed to the action of heat, it volatilizes completely in pungent vapors, which are inflammable and burn with a blue flame. It is miscible with water in all proportions; it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. The hydrate of acetic acid is soluble also in alcohol.

2. The acetates undergo decomposition at a red-heat; among the products of this decomposition, we find generally acetic acid, and invariably acetone. The acetates of the alkalies and alkaline earths are converted into carbonates, in this process. Many of the acetates with metallic base leave the metal behind in its pure state, others leave it in the form of oxide. The whole of the residues which the acetates leave upon ignition are carbonaceous. Nearly the whole of the acetates dissolve in water and in alcohol; most of them dissolve readily in water, and a few only are difficult of solution in this menstruum.

3. If *perchloride of iron* be added to acetic acid, and the acid be then saturated with ammonia, or if a neutral acetate be mixed with perchloride of iron, the solution will acquire a deep dark red tint, owing to the ensuing formation of PERACETATE OF IRON. Ammonia precipitates the whole of the peroxide of iron from this solution.

4. Neutral acetates (but not free acetic acid) yield with *nitrate*

of silver, white crystalline precipitates of ACETATE OF SILVER, ($Ag O, \bar{A}$,) which are very sparingly soluble in cold water. They dissolve more readily in hot water, but separate again, upon cooling, in the form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

5. *Protonitrate of mercury* produces in solutions of acetic acid, and more readily still in solutions of acetates, white scaly crystalline precipitates of PROTACETATE OF MERCURY, ($Hg_2 O, \bar{A}$), which are sparingly soluble in water and acetic acid, in the cold, but dissolve readily in an excess of the precipitant. Protacetate of mercury dissolves in water upon the application of heat, but separates again upon cooling, in the form of small crystals; in this process, the protacetate of mercury undergoes partial decomposition, a portion of the mercury separates in the metallic state, and imparts a grey color to the precipitate. When the protacetate of mercury is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. When acetates are heated with *dilute sulphuric acid*, ACETIC ACID is evolved, which may be detected by its pungent odor. But when the acetates are heated with a mixture of equal portions of *concentrated sulphuric acid* and *alcohol*, ACETIC ETHER ($C_4 H_5 O, \bar{A} = Ae O, \bar{A}$) is evolved. The odor of this ether is highly characteristic and agreeable; it is particularly perceptible upon agitating the mixture when somewhat refrigerated, and is hardly liable to lead to mistakes, at any rate far less so than the pungent odor of the free acetic acid.

7. If acetates be distilled with dilute sulphuric acid, and the distillate be subsequently digested with an excess of oxide of lead, part of the latter will dissolve as a basic acetate of lead, which may be readily detected by its alkaline reaction.

b. FORMIC ACID. ($C_2 H O_3 = Fo O_3$.)

1. The hydrate of formic acid is a colorless, pellucid, slightly

fuming liquid of a characteristic and exceedingly penetrating odor. When cooled to below 32°, it crystallizes in colorless plates. It is miscible in all proportions with water and with alcohol. When exposed to the action of heat, it volatilizes completely; the vapor is inflammable and burns with a blue flame.

2. The formiates, like the corresponding acetates, leave upon ignition, either carbonates, or oxides, or metals, behind, the process being attended, moreover, with separation of charcoal and evolution of carburetted hydrogen, carbonic acid, and water. All the compounds of formic acid with bases are soluble in water; alcohol likewise dissolves some of them, but fails to dissolve others.

3. Formic acid presents the same deportment with *perchloride of iron* as acetic acid.

4. *Nitrate of silver* fails to precipitate free formic acid, and precipitates alkaline formiates, only from concentrated solutions. The white, sparingly soluble, crystalline precipitate of FORMIATE OF SILVER, ($Ag\,O, Fo\,O_3$,) acquires very speedily a deeper tint, owing to the separation of metallic silver. This reduction of the oxide of silver to the metallic state takes place, even in the cold, after the lapse of some time, and immediately upon applying heat to the fluid containing the precipitated formiate of silver. The same reduction of the oxide of silver to the metallic state is observed even in solutions of free formic acid and in solutions of formiates, which are so dilute, that the addition of the nitrate of silver fails to produce a precipitate. The rationale of this reduction is as follows: the formic acid, which may be looked upon as a compound of carbonic oxide with water, deprives the oxide of silver of its oxygen, causing thus the formation of carbonic acid, which escapes, and of water, whilst the reduced silver separates in the metallic state.

5. *Protonitrate of mercury* fails to precipitate solutions of free formic acid; but in concentrated solutions of alkaline formiates, this reagent produces a white, sparingly soluble precipitate of PROTOFORMIATE OF MERCURY, ($Hg_2\,O, Fo\,O_3$), which turns very

speedily grey, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time; but this reduction is immediate when heat is applied to the fluid containing the precipitate. This reduction likewise is attended with the formation of carbonic acid and water, and takes equally place in solutions of free formic acid, and in fluids which are so highly dilute that the protoformiate of mercury is retained in solution, instead of precipitating.

6. If formic acid or an alkaline formiate be heated to from 140° to 158° with *perchloride of mercury*, PROTOCHLORIDE OF MERCURY will precipitate. If the mixture be heated to the boiling point of water, metallic mercury will separate in conjunction with the protochloride.

7. When formic acid or a formiate is heated with *concentrated sulphuric acid*, the formic acid is resolved into water, and carbonic oxide gas, which escapes with effervescence, and when kindled, burns with a blue flame. The mixture does not turn black in this process. The rationale of this decomposition of the formic acid is this: the sulphuric acid withdraws from the formic acid the water or the oxide necessary for the existence of the latter acid, and occasions thus a transposition of its elements ($C_2 H O_3 = 2 C O + H O$). Upon heating a formiate with dilute sulphuric acid, formic acid escapes, which may be readily detected by its odor. When a formiate is treated with a mixture of sulphuric acid and alcohol, formic ether is evolved, which is characterized by its peculiar arrack-like smell.

Recapitulation and remarks.—The reactions of acetic acid and formic acid are not so characteristic as those of many other acids; the positive detection of these two acids is accordingly to be based only upon the concurrence of all the various reactions which I have given. The odor of acetic acid and that of acetic ether form the most ready, its deportment with oxide of lead, the most positive test, for acetic acid. Formic acid is to be detected best by its behaviour with sulphuric acid and with the salts of the noble metals. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of peroxide of mercury, or of oxide of silver The formic acid reduces the oxides, and suffers decomposition, being resolved into carbonic oxide and water ; whilst the acetic acid combines with the oxides to acetates which remain in solution.

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

PART II.

PRELIMINARY REMARKS

ON THE

COURSE OF QUALITATIVE ANALYSIS IN GENERAL

AND ON THE

PLAN OF THIS PART OF THE PRESENT WORK IN PARTICULAR.

THE knowledge of the reagents and of the deportment which other bodies exhibit with them, enables us to ascertain at once whether some compound or other of which the physical properties permit an inference to its nature, is in reality what we take it to be. Thus, for instance, a few simple reactions convince us that a body which we suppose to be calcareous spar, is really carbonate of lime, and that another, which we deem gypsum, is really sulphate of lime. This knowledge suffices usually also to ascertain, whether a certain body is present or not in some compound or other; for instance, whether a white powder contains protochloride of mercury or not. But if our design is to ascertain the chemical nature of a substance entirely unknown to us,—if we wish to discover *all* the constituents of a mixture or chemical compound,—if we intend to prove that, besides certain bodies which we have detected in a mixture or compound, no other substance can be present,—consequently, if a COMPLETE QUALITATIVE ANALYSIS is our object, the mere knowledge of the reagents, and of the reactions of other bodies with them, will not suffice for the attainment of this end; this requires the additional knowledge of a systematic and progressive course of analysis, in other words, the knowledge of the *order* and *succession* in which solvents and general and special reagents ought to be applied to effect the speedy and safe detection of every individual component of a compound or mixture, and to arrive at the positive body of the absence of all other substances. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method whatever in our investigations and experiments, analyzing becomes (at least in the hand of a novice) mere guess work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances, will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances present, or supposed to be present, in a compound or mixture, are, in the first place to be classed into certain groups, which are then again to be subdivided until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order and succession in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a certain definite course or system of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every case imaginable, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will, in certain given cases, most readily and rapidly lead to the attainment of the object in view.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining the greatest possible simplicity with the greatest possible security, is the object of the second part of this work.

The elements and compounds comprised in it, are the same which I have enumerated in my preliminary remarks.

The construction of a universally applicable systematic course of analysis requires due regard to, and provision for, every contingency that may possibly arise; it is accordingly self-evident that the various substances treated of—(however mixed and intermixed with one another we may imagine them to be)—must be supposed free from extraneous organic matters, since the presence of such matters prevents the manifestation of many reactions, and causes various modifications in others. I do not by any means intend to assert here that the proposed systematic course may not be exactly followed even in presence of many organic substances, especially of such as dissolve in water to colorless or clear fluids. Experience and due reflection in every individual case will best instruct the young chemist how to act in cases where dark coloring or slimy matters happen to be present. For the most important rules, and the method in general, I refer to § 132.

This part of the work is divided into two sections; the first contains PRACTICAL INSTRUCTIONS IN ANALYSIS, wherein I have laid down a systematic course which, progressing step by step, must finally lead to the end in view. At first sight, many parts of it may perhaps be deemed rather prolix; I think, however, that it would have scarcely been possible to abbreviate it, except at the expense of that clearness and perspicuity which are so indispensible to render a work of this description really useful to the young student. I hope, moreover, that my readers will soon become convinced by experience that this prolixity, after all, does not prove any serious bar to the celerity with which the systematic course may be gone through, since I have invariably arranged the phenomena which may occur, into clearly characterised cases, so that the student, having to look simply and exclusively to the respective case under his consideration, and one number always referring to the other, may save himself the trouble of reading through those parts which do not bear upon the particular case engaging his attention.

The subdivisions of this practical course are, 1. Preliminary examination; 2. Solution; 3. Actual examination; 4. Confirmatory experiments.

The third subdivision (the actual examination) is again subdivided into, 1. Examination of compounds in which but one basic and one acid are assumed to be present; and, 2. Examination of mixtures or compounds in which all the substances treated of in the present work are assumed to be present. With respect to the latter section I have to remark that where the preliminary examination has not afforded the most positive conviction of the absence of certain groups of substances, the student cannot safely disregard any paragraph referred to, in consequence of the phenomena that manifest themselves. In cases where it is simply intended to test a compound or mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular numbers which ought to be attended to.

The second section contains an EXPLANATION OF THE PRACTICAL PROCESS: an exposition of the principles whereon the separation, and of the causes, whereon the detection of substances depend; it contains, moreover, various additions to the first section. Students will do well to make themselves early acquainted with this part, which may be properly considered as a key to the first section.

As appendix I give, 1. A GENERAL PLAN OF THE ORDER AND SUCCESSION IN WHICH I WOULD RECOMMEND THE YOUNG STUDENT TO ANALYSE SUBSTANCES FOR PRACTICE; 2. INSTRUCTIONS HOW TO ARRANGE THE RESULTS OF HIS INVESTIGATION IN THE MOST ADVANTAGEOUS MANNER; and 3. A TABULAR ARRANGEMENT OF THE MORE FREQUENTLY OCCURRING FORMS AND COMPOUNDS

OF THE SUBSTANCES ENUMERATED IN MY PRELIMINARY REMARKS, BASED MORE PARTICULARLY UPON THEIR RESPECTIVE DEGREE OF SOLUBILITY IN WATER AND ACIDS. The first is intended to serve the pupil as a guide in his efforts to acquire a sound and thorough knowledge of qualitative analysis; the second is intended to afford him a means of obtaining a clear view over the whole domain of the science; and the third will certainly prove useful to many who are not yet quite conversant with the various degrees of solubility of substances, particularly when required to determine the manner the acids, bases, &c., detected in the course of an analysis, were originally combined in the examined substance, or what particular acid or acids cannot possibly co-exist with certain bases in aqueous or acid solutions.

In compliance with the expressed wishes of many parties, I have added to this edition a chapter treating of the REACTIONS OF THE MORE FREQUENTLY OCCURRING ALKALOIDS, and containing a well-tried method to effect their detection in the systematic course of analysis.

FIRST SECTION.

PRACTICAL PROCESS.

I. PRELIMINARY EXAMINATION.

§ 106.

The operator has, in the first place, to examine the physical properties—(color, shape, hardness, gravity, odor, &c.)—of the substance which he intends to analyse, since these will often enable him in some measure to infer the nature of the said substance. Before proceeding to the application of any chemical process, the operator should invariably consider how much of the substance to be analysed he has at command, since it is necessary, at this early period of the examination, to calculate the quantity which may be spent in the preliminary investigation. A reasonable economy is in all cases advisable, though we may possess the substance in large quantities; and it must be laid down as a fixed rule, never to use at once the whole of what we possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments.

§ 107.

A. THE BODY UNDER EXAMINATION IS SOLID.

I. IT IS NEITHER A PURE METAL NOR AN ALLOY.

1. The substance is fit for examination when in powder or in minute crystals; but when in larger crystals or in solid pieces, it is necessary in the first place to reduce a portion of it to powder, if possible.

2. The powder is heated in a small iron spoon, over a spirit-lamp; the resulting phenomena may lead to many positive or probable conclusions regarding the nature of the substance.

a. THE SUBSTANCE REMAINS UNALTERED: absence of organic substances, salts containing water, readily fusible matters, and volatile bodies.

b. IT FUSES READILY AND RE-SOLIDIFIES WITH EXPULSION OF AQUEOUS VAPOR: salts which contain water of crystallization If the solidified residue fuses again upon the application of an increased heat, *c* must be had regard to.

c. IT FUSES WITHOUT EXPULSION OF AQUEOUS VAPOR. A small piece of paper is added to the melting mass; if deflagration takes place, this indicates the presence of NITRATES, or also of the more rarely occurring CHLORATES.

d. IT VOLATILIZES COMPLETELY OR PARTLY. In the first case, no fixed bases are present; in the latter, the substance contains a volatile body in admixture.

α. No odor is emitted. In this case we have to look more particularly for compounds of AMMONIA, MERCURY, and ARSENIC.

β. An odor is emitted. If the odor is that of sulphurous acid, SULPHUR is present; if that of iodine, and if the vapors are violet, the presence of free IODINE is certain. With equal certainty free BENZOIC ACID, and many other substances, may be detected by the odor of their vapors.

e. THE SUBSTANCE IS A WHITE POWDER, TURNING YELLOW UPON THE APPLICATION OF HEAT; this indicates OXIDE OF ZINC, OXIDE OF LEAD, OR OXIDE OF BISMUTH; the oxide of zinc resumes its white color upon cooling, but the oxide of lead and oxide of bismuth remain yellow.

f. CARBONIZATION TAKES PLACE: organic substances. If the residue effervesces when drenched with acids, whilst the original substance does not present that property, this indicates the presence of ORGANIC ACIDS, combined with alkalies or alkaline earths. Odor of cyanogen indicates the presence of a CYANIDE.

Many substances, moreover, swell up considerably upon the application of heat; such are, for instance, borax, sulphate of alumina, &c.; others decrepitate, e. g. chloride of sodium, and chloride of potassium, &c.: these phenomena, however, are of a less conclusive nature than the preceding.

3. A small portion of the substance is put on a charcoal support, and exposed to the reducing flame of the blow-pipe. Since most of the phenomena just now described (2) are equally produced by this process, I will enumerate here only those which result more particularly and exclusively from its application.

a. THE SUBSTANCE VOLATILIZES PARTLY OR COMPLETELY. This indicates, besides the substances mentioned in § 107. 2. *d.*, also OXIDE OF ANTIMONY, and several other oxides. (Compare § 107. 3. *d.* *β.*) The oxide of antimony fuses previously to volatilizing in the form of a white vapor. The presence of ARSENIOUS OR ARSENIC ACID is indicated by the emission of the characteristic odor of garlic, which is rendered more strongly perceptible by adding the carbonate of soda to the sample previously to exposing it to the blow-pipe flame.

b. THE BODY FUSES, AND IS IMBIBED BY THE CHARCOAL; this indicates the presence of ALKALIES. In this case, a portion of the finely levigated substance is placed upon the moistened loop of a platinum wire, and the point of the inner flame is directed upon it. If the oxidizing flame assumes a violet tint, this indicates the presence of POTASS alone; if a yellow tint, the presence of SODA, with which potass may, however, be admixed, even in considerable proportion, since the flame appears invariably yellow when both these alkalies are present.

c. THE SUBSTANCE LEAVES AN INFUSIBLE WHITE RESIDUE ON THE CHARCOAL, EITHER AT ONCE, OR AFTER PREVIOUS MELTING IN THE CRYSTALLIZATION WATER; this indicates more particularly the presence of barytes, strontia, lime, magnesia, alumina, zinc, and silicic acid. Among these substances, STRONTIA, LIME, MAGNESIA, and ZINC, are distinguished by strong luminousness in the blow-pipe flame. The white residue is touched with a drop of solution of protonitrate of cobalt, and is then again strongly ignited. If the mass assumes a fine blue tint, this indicates the presence of ALUMINA; if a reddish tint, of MAGNESIA; if a green color, of ZINC. When SILICIC ACID is present, the mass also assumes a faint bluish tint, which should not be confounded with that proceeding from the presence of alumina. Silicic acid is characterized moreover by the formation of a clear button which ensues, attended with effervescence, upon exposing this acid, with carbonate of soda, to a strong blow-pipe flame. (§ 100. *b.*)

d. THE SUBSTANCE LEAVES AN INFUSIBLE RESIDUE OF A DIFFERENT COLOR, OR A REDUCTION TO THE METALLIC STATE TAKES PLACE, WITH OR WITHOUT INCRUSTATION OF THE CHARCOAL SUPPORT. A portion of the powder is mixed with carbonate of soda, and heated on charcoal in the reducing flame.

α. The continued application of a strong blast produces a metallic grain, without incrustation of the charcoal; this indicates the presence of GOLD, SILVER, TIN, or COPPER. Platinum, iron, cobalt, and nickel, are likewise reduced, but yield no metallic grains.

β. The charcoal support is coated over with an incrustation, either with or without simultaneous formation of a metallic grain; this indicates the presence of bismuth, lead, cadmium, antimony, or zinc.

aa. If the incrustation is white, ANTIMONY OR ZINC may be supposed to be present. The incrustation produced by zinc appears yellow as long as it remains hot. The pure metallic grain of antimony continues to evolve white vapors, even for a long time after all application of heat has been withdrawn, and generally becomes at last, upon cooling, surrounded with crystals of oxide of antimony. It is brittle under the stroke of the hammer.

bb. The incrustation is more or less yellow or brown; this indicates the presence of BISMUTH, LEAD, or CADMIUM. The yellow incrustation of oxide of cadmium inclines slightly to orange; the brownish-yellow incrustations of oxide of lead and oxide of bismuth change to a light yellow upon cooling. Cadmium volatilizes immediately upon reduction. The grains of lead are very malleable, whilst the grains of bismuth are brittle under the stroke of the hammer.

The student must be prepared of course, to meet with the manifestation of mixed phenomena, arising from the intermixture, or combination of many different substances, and he must therefore be guarded in his conclusions, since it is impossible to give defined and characterized cases, which will offer at the same time, the advantage of general applicability.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. A small portion of the substance is heated with water, acidulated with acetic acid.

a. HYDROGEN GAS IS EVOLVED; this indicates the presence of a light metal. The presence of alkalies and of alkaline earths must be had regard to in the actual examination.

b. NO HYDROGEN IS EVOLVED; this indicates the absence of light metals. Alkalies and alkaline earths may be altogether disregarded in the course of the special investigation.

2. A portion of the substance is heated on charcoal, in the reducing flame of the blow-pipe, and the ensuing phenomena are carefully watched; whether the substance fuses, for instance, whether an incrustation is formed, whether an odor is emitted, &c.

a. THE SUBSTANCE REMAINS UNALTERED; this is pretty conclusive of the absence of antimony, zinc, lead, bismuth, cadmium, tin, mercury, and arsenic; the absence of gold, silver, and copper, is also probable; it indicates the presence of PLATINUM, IRON, MANGANESE, NICKEL, or COBALT.

b. THE SUBSTANCE FUSES WITHOUT SIMULTANEOUS INCRUSTATION, AND WITHOUT ODOR; this indicates the absence of antimony, zinc, lead, bismuth, cadmium, and arsenic, and the presence of GOLD, SILVER, COPPER, or TIN.

c. THE SUBSTANCE FUSES, AND AN INCRUSTATION IS FORMED, BUT NO ODOR EMITTED; this indicates the absence of arsenic, and the presence of ANTIMONY, ZINC, BISMUTH, LEAD, or CADMIUM. (Compare § 107. I. 3. *d.* *β.*)

d. THE SUBSTANCE EMITS THE ODOR OF GARLIC; this indicates the presence of ARSENIC. For the other phenomena which may manifest themselves, I refer to *a.* *b.* or *c.*

3. A portion of the substance is heated before the blow-pipe in a glass tube, sealed at one end.

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE; this indicates the absence of mercury.

b. A SUBLIMATE IS FORMED; this indicates the presence of MERCURY, CADMIUM, or ARSENIC. The sublimate of mercury which consists of small globules, cannot possibly be confounded with the sublimate of cadmium or arsenic.

§ 108.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. A small portion of the fluid is evaporated in a platinum spoon, or in a small porcelain crucible, to ascertain in the first place whether the fluid contains any matter in solution; the nature of the residue is then examined according to the directions given at § 107.

2. The fluid is tested with litmus papers (blue and reddened).

a. THE FLUID REDDENS BLUE LITMUS PAPER. This reaction may be caused by a free acid, an acid salt, or by a soluble metallic salt. In order to distinguish between these cases, a small quantity of the liquid is poured into a watch-glass, and a little rod placed in it, the extreme point of which has previously been dipped into dilute solution of carbonate of potass; if the fluid remains clear, or if the precipitate which may form at first, redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes and remains turbid, this generally proves the presence of a soluble metallic salt. As a matter of course, a solution which contains a free acid or an acid salt can no longer be considered simply aqueous, and the subsequent examination must accordingly proceed with due regard to the possible presence of substances insoluble in water but soluble in acids.

b. REDDENED LITMUS PAPER TURNS BLUE; this indicates the presence of free alkalies or alkalines carbonate, free alkaline earths, alkaline sulphurets, and of a number of other salts. Substances dissolved in fluids containing a free alkali, may belong to the class of acids soluble in water as well as to that of bodies insoluble in that menstruum. The way in which this point is to be settled, and further information on the subject of alkaline solutions in general, will be found at § 117. I. 2.

3. The fluid is examined by smelling and tasting, or, should this fail to yield satisfactory results, by distillation, whether the simple solvent present is water, alcohol, ether, &c. If it is found not to be water, the solution is evaporated to dryness, and the residue treated according to § 107.

4. If the solution happens to be aqueous, and manifests an acid reaction, a portion of it is highly diluted with water. If this addition of water to the fluid imparts a milky and turbid appearance to the latter, the presence of ANTIMONY, BISMUTH, OR TIN, may be inferred. If the precipitate disappears upon the addition of tartaric acid, we may conclude that antimony is present, whilst its persistence with tartaric, and re-solution by acetic acid, indicates the presence of bismuth. The original fluid is then treated either as directed at § 110, or at § 117, according to whether the operator has reason to suppose it to be the solution of a simple, or that of a compound, or mixed substance.

II. SOLUTION OF BODIES OR CLASSIFICATION OF SUBSTANCES ACCORDING TO THEIR DEPORTMENT WITH CERTAIN SOLVENTS.

§ 109.

Water and hydrochloric acid, or in certain cases nitric acid, are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective deportment with these solvents.

First class. SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC OR NITRIC ACID.

Third class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE, IN WATER AND HYDROCHLORIC OR NITRIC ACID.

The solution of alloys being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for alloys. (vide B.)

The process of solution or separation is conducted in the following manner.

A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

1. About fifteen or twenty grains of the finely levigated substance under examination, are covered in a test-tube with from ten to twelve times the amount of distilled water, and the mixture is heated to boiling over a spirit-lamp.

a. THE SUBSTANCE DISSOLVES COMPLETELY. In this case it belongs to the first class; regard must be had to what has been stated in § 108. 2. concerning reactions. The solution is treated either as directed at § 110, or as directed at § 117, as either one or several acids and bases are supposed to be present.

b. A RESIDUE REMAINS EVEN AFTER PROTRACTED BOILING OF THE SOLUTION. The residue is allowed to subside, and the fluid filtered off if possible in such a manner as to leave the residue in the test-tube; a few drops of the clear filtrate are then evaporated on a clean platinum plate; if no residue remains, the substance is completely insoluble in water, and is then further treated as directed at § 109. 2. But if a residue remains, the substance is at least partly soluble. The original residue is in that case boiled once more with water, the fluid is filtered off, and the filtrate finally added to the original solution, which is then treated, according to circumstances, either as directed at § 110, or as directed at § 117. The residue is washed with water, and subsequently treated in conformity with the directions of § 109. 2.

2. The residue of 1. is drenched with dilute hydrochloric acid. Should this fail to dissolve it, the mixture is to be heated to the boiling point, and should even this fail to effect a perfect solution, the fluid is to be decanted, and the residue boiled with concentrated hydrochloric acid.

The phenomena which may manifest themselves in this operation, and which ought to be carefully observed are, α. Effervescence, which indicates the presence of carbonic acid, or sulphuretted hydrogen, (vide § 111. 2.); β. Evolution of chlorine, which indicates the presence of hyperoxides, chromates, &c.; γ. Emission of the odor of hydrocyanic acid, which indicates the presence of insoluble cyanides. Since the latter are more appropriately decomposed in a different way from that pursued in the case of other substances, a special paragraph will be devoted to them. (Vide § 131.)

a. THE RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID; the solution is treated, according to circumstances, either as directed at § 113, or as directed at § 117. II. The substance belongs to the second class.

Substances which when tested with hydrochloric acid, leave simply a residue of undissolved sulphur which is readily recognized by its color and specific weight, belong also to the second class, and are treated accordingly.

b. A RESIDUE REMAINS. In this case the test-tube containing the specimen which has been boiled with the hydrochloric acid, is put aside pro tempore, and another portion of the substance under examination is boiled with nitric acid, with subsequent addition of water.

α. *The specimen is completely dissolved, or sulphur alone remains undissolved;* the body in these cases also belongs to the second class; this solution is then further tested for bases, according to circumstances, either as directed § 113, or in conformity to the directions of § 117. III.

β. *A residue remains.*

aa. THE OPERATOR HAS REASON TO SUPPOSE THAT THE SUBSTANCE UNDER EXAMINATION CONTAINS ONLY *ONE* BASE AND *ONE* ACID. The substance is drenched with aqua regia, and heat applied.

αα. The substance dissolves. The solution is treated according to § 113.

ββ. The substance does not dissolve. In that case the operator has to proceed according to the directions given at § 116.

bb. THE OPERATOR HAS REASON TO SUPPOSE THAT THE SUBSTANCE UNDER EXAMINATION IS A COMPLEX COMPOUND OR MIXTURE. In this case the reserved hydrochloric solution (§ 109. A. 2. *b.*) is tested for the bases. It is for this purpose heated to boiling with the insoluble residue—(which latter is subsequently to be treated as directed at § 109. 3)—and filtered hot into a tube containing some water; the residue is then again boiled with some water, and the fluid subsequently filtered off hot, and added to the hydrochloric acid solution.

αα. The filtrate becomes turbid and milky; this indicates ANTIMONY and BISMUTH; or it deposits fine crystals: this indicates the presence of LEAD. The filtrate is heated (if needed, with the addition of some hydrochloric acid) until it clears again; the further process is conducted according to the directions of § 117. II.

ββ. The filtrate remains clear. A few drops of it are evaporated to ascertain beyond doubt whether the hydrochloric acid has really dissolved anything. Should a residue remain, the filtrate is treated according to § 117. II.

3. Should the boiling concentrated hydrochloric acid have left a residue, this is washed with water, and treated as directed § 130.

B. THE SUBSTANCE UNDER EXAMINATION IS A METAL OR AN ALLOY.

The metals are best divided according to their deportment with nitric acid.

I. METALS WHICH ARE NOT AFFECTED BY NITRIC ACID: gold, platinum.

II. METALS WHICH ARE OXIDIZED BY NITRIC ACID, BUT OF WHICH THE OXIDES DO NOT DISSOLVE IN AN EXCESS OF THE ACID: antimony, tin.

III. METALS WHICH ARE OXIDIZED BY NITRIC ACID, AND OF WHICH THE OXIDES DISSOLVE TO NITRATES IN AN EXCESS OF THE ACID: all other metals.

Nitric acid of 1.25 sp. gr. is poured over the metal or alloy under examination, and heat applied.

1. COMPLETE SOLUTION TAKES PLACE EITHER AT ONCE OR UPON THE ADDITION OF WATER: this proves the absence of (platinum) gold, antimony, and tin: a small portion of the solution is diluted with a copious amount of water.

a. The solution remains clear; some hydrochloric acid is added. If this produces a white precipitate, which does not redissolve upon heating the fluid, but is dissolved by ammonia, after previous washing, SILVER is present. The original solution is treated, as directed at § 118.

b. The solution becomes turbid and milky; this indicates the presence of BISMUTH. The solution is filtered, and the filtrate tested for silver, as at *a.* The original solution is finally treated according to § 118.

2. A RESIDUE REMAINS.

a. A metallic residue remains. The solution is filtered, and the filtrate treated as directed at § 109. B. 1., after having examined, in the first place, whether anything has been dissolved. The residue is thoroughly strained, and subsequently dissolved in aqua regia; the solution is divided into two portions, and chloride of potassium added to the one: if a yellow precipitate is formed, this indicates the presence of PLATINUM. Protosulphate of iron is added to the other portion: if a black precipitate is formed, this indicates the presence of GOLD.

b. A white pulverulent residue remains; this indicates the presence of ANTIMONY and TIN. The solution is filtered, and the filtrate treated as directed at § 109. B. 1., after having examined, in the first place, whether anything has been dissolved. The residue is thoroughly washed, and heated subsequently with a hot saturated solution of bitartrate of potass, or with a solution of tartaric acid.

α. Complete solution takes place: this indicates the presence of oxide of ANTIMONY alone; the solution is tested with sulphuretted hydrogen.

β. A white precipitate remains, even after boiling with a fresh portion of solution of bitartrate of potass or tartaric acid; this indicates the probable presence of TIN. The solution is filtered and the filtrate mixed, in the first place, with some hydrochloric acid, and subsequently with solution of sulphuretted hydrogen. If an orange-red precipitate is formed, OXIDE OF ANTIMONY is present. It is invariably necessary that the operator should satisfy himself whether the residue consists really of peroxide of tin; this may be clearly ascertained by mixing the residue with cyanide of potassium and carbonate of soda, and reducing it before the blow-pipe. (Compare § 95. *c.* 7.)

III. ACTUAL EXAMINATION.

Compounds supposed to consist simply of one base and one acid; or of one metal and one metalloid.

A. SUBSTANCES SOLUBLE IN WATER.

Detection of the base.[*]

§ 110.

1. Some hydrochloric acid is added to a portion of the aqueous solution.

a. NO PRECIPITATE IS FORMED; this is a positive proof of the absence of silver and protoxide of mercury, and is likewise a probable indication of the absence of lead. The acidified solution is treated according to the directions of § 110. 2.

b. A PRECIPITATE IS FORMED. Divide the fluid, in which the precipitate is suspended, into two portions, and add ammonia in excess to the one.

α. *The precipitate redissolves, and the fluid becomes clear;* this shows the precipitate to have consisted of chloride of silver, and is consequently indicative of the presence of SILVER. To arrive at a positive conviction on this point, the original solution must be tested with chromate of potash, and with sulphuretted hydrogen. (Vide § 91. *a.* 3, and 97. *b.* 6.)

β. *The precipitate becomes black;* this shows the precipitate to have consisted of protochloride of mercury, which has now been converted by the ammonia into protoxide of mercury; it is consequently indicative of the presence of PROTOXIDE OF MERCURY. To set all doubt on this point at rest, the original solution is tested with protochloride of tin and with metallic copper. (Vide § 91. *b.*)

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[*] We include here arsenious and arsenic acid.

γ. *The precipitate remains unaltered;* it consists in this case of chloride of lead, which is neither decomposed nor dissolved by ammonia; this reaction is accordingly indicative of the presence of LEAD. Whether the precipitate consists really of chloride of lead or not is conclusively ascertained: 1st, by diluting the second portion of the fluid in which the precipitate produced by hydrochloric acid is suspended, with a copious amount of water and applying heat; the precipitate must dissolve if it consists really of chloride of lead; and 2nd, by adding dilute sulphuric acid to the original solution, (§ 91. *c.*)

2. The acidified fluid of 1. *a.* is mixed with solution of sulphuretted hydrogen until it smells distinctly of that gas, even after continued agitation; heat is subsequently applied to the mixture.

a. THE FLUID REMAINS CLEAR. Pass over to 3, since this is a proof that lead, bismuth, copper, cadmium, peroxide of mercury, gold, platinum, tin, antimony, arsenic, and peroxide of iron, are not present.

b. A PRECIPITATE IS FORMED.

α. THIS PRECIPITATE IS WHITE; it consists in this case of separated sulphur, and is indicative of the presence of PEROXIDE OF IRON (§ 89. *f.*) However, as the separation of sulphur may also be caused by other substances, it is indispensable that the operator should satisfy himself whether the substance present is really peroxide of iron or not. For this purpose the original solution is to be tested with ammonia, and with ferrocyanide of potassium.

β. THE PRECIPITATE IS YELLOW; in this case it may consist either of sulphuret of cadmium, or sulphuret of arsenic, or bisulphuret of tin; it indicates accordingly presence of either cadmium, or arsenic, or peroxide of tin. To distinguish between them, ammonia in excess is added to a portion of the fluid, wherein the precipitate is suspended.

aa. The precipitate does not disappear; it consists of CADMIUM; for sulphuret of cadmium is insoluble in ammonia. The blow-pipe is finally resorted to as a confirmatory test. (§ 92. *d.*)

bb. The precipitate disappears. It consists either of peroxide of tin or of arsenic. Ammonia is added to a portion of the original solution.

αα. A white precipitate is formed. PEROXIDE OF TIN is the substance present. Positive conviction is obtained by reducing the precipitate before the blow-pipe, with cyanide of potassium and carbonate of soda. (§ 95. *c.*)

ββ. No precipitate is formed. This indicates the presence of ARSENIC. Positive conviction may be arrived at by the production of an arsenical mirror which is effected by reducing the original substance, or the precipitated sulphuret of arsenic, with cyanide of potassium and carbonate of soda, or in some other way; and by exposing the original substance with carbonate of soda to the inner flame of the blow-pipe. (§ 95. *d.*)

γ. THE PRECIPITATE IS ORANGE-COLORED; in this case it consists of sulphuret of antimony, and indicates the presence of OXIDE OF ANTIMONY. Reduction before the blow-pipe is resorted to for confirmation. (§ 95. *a.*)

δ. THE PRECIPITATE IS BROWN. It consists of protosulphuret of tin, and indicates the presence of PROTOXIDE OF TIN. To remove all doubt on this point, one portion of the original solution is tested with solution of perchloride of mercury, and another with solution of perchloride of gold. (§ 95. *b.*)

ε. THE PRECIPITATE IS BLACK. It may in this case consist either of sulphuret of lead, sulphuret of copper, sulphuret of bismuth, sulphuret of gold, sulphuret of platinum, or bisulphuret of mercury. To distinguish between these different sulphurets, the following experiments are to be had recourse to.

aa. Dilute sulphuric acid is added to a portion of the original solution: a white precipitate is formed; this indicates LEAD. Chromate of potass is employed as a conclusive test. (§ 91. *c.*)

bb. Ammonia in excess is added to a portion of the original solution. A blue precipitate is formed which redissolves in an excess of the precipitant, imparting an azure color to the fluid; this indicates COPPER. Ferrocyanide of potassium is resorted to as a conclusive test. (§ 92. *b.*)

cc. Potass is added to a portion of the original solution; a yellow precipitate is formed; this indicates PEROXIDE OF MERCURY. Protochloride of tin and metallic copper are applied as conclusive tests. (§ 92. *a.*) The presence of peroxide of mercury is usually sufficiently indicated by the several changes of color through which the precipitate produced by the sulphuretted hydrogen water in the fluid under examination is observed to pass; this precipitate is white at first, but passes subsequently, upon the addition of an excess of the precipitant, through yellow and orange, and turns finally black. (§ 92. *a.* 3.)

dd. A portion of the original solution is evaporated nearly to dryness, in a porcelain crucible, and the residue rinsed into a test-tube, half filled with water. If the solution becomes milky, a basic salt of bismuth is present; this reaction, consequently, indicates BISMUTH. The blow-pipe is resorted to as a conclusive test. (§ 92. *c.*)

ee. Solution of protosulphate of iron is added to a portion of the original solution. A fine black precipitate is indicative of the presence of GOLD. To remove all doubt as to the nature of this precipitate, the blow-pipe is resorted to; or the original solution is tested with protochloride of tin. (§ 94. *a.*)

ff. Chloride of potassium is added to a portion of the original solution; the formation of a yellow crystalline precipitate is indicative of the presence of PLATINUM. To remove all doubt on this point, the precipitate is ignited. (§ 94. *b.*)

3. A portion of the original solution is mixed with sal ammoniac, and ammonia is subsequently added to alkaline reaction; hydrosulphuret of ammonia is then finally added, no matter whether a precipitate did form upon the addition of the ammonia or not.

a. NO PRECIPITATE IS FORMED; pass over to § 110. 4.; for iron, cobalt, nickel, manganese, zinc, chromium, and alumina are not present.

b. A PRECIPITATE IS FORMED.

α. *The precipitate is black;* protoxide of iron, nickel, or cobalt. A portion of the original solution is mixed with caustic potass.

aa. A dirty greenish-white precipitate is formed, which soon changes to a reddish-brown, when exposed to the air: PROTOXIDE OF IRON. Ferricyanide of potassium is resorted to as a conclusive test. (§ 89. *e.*)

bb. A precipitate of a light greenish tint is produced, which does not change its color: NICKEL. Ammonia, with subsequent addition of potass, is resorted to as a conclusive test. (§ 89. *c.*)

cc. A sky-blue precipitate is formed, which, upon boiling, becomes reddish: COBALT. The blow-pipe is resorted to as a conclusive test. (§ 89. *d.*)

β. *The precipitate is not black.*

aa. If the precipitate is distinctly flesh-colored, it consists of sulphuret of manganese, and is consequently indicative of the presence of PROTOXIDE OF MANGANESE. The addition of potass to the original solution, or the blow-pipe, are resorted to as conclusive tests. (§ 89. *b.*)

bb. If the precipitate is bluish-green, it consists of hydrated OXIDE OF CHROMIUM. The addition of potass to the original solution, and the blow-pipe, are resorted to as conclusive tests. (§ 88. *b.*)

cc. If the precipitate is white, it may consist either of hydrate of alumina, or of sulphuret of zinc, and thus indicate the presence of either alumina or oxide of zinc. To distinguish between these two oxides, solution of potass is gradually dropped into a portion of the original solution, till the precipitate which forms at first is redissolved; and

αα. Solution of sulphuretted hydrogen is then added to a portion of this solution; the formation of a white precipitate indicates the presence of ZINC. As a conclusive test, the reaction with solution of protonitrate of cobalt before the blow-pipe is selected. (§ 89. *a.*)

ββ. Chloride of ammonium is added to another portion of the potass solution. The formation of a white precipitate indicates the presence of ALUMINA. The test with solution of protonitrate of cobalt before the blow-pipe is conclusive. (§ 88. *a.*)

Note to § 110. 3. *b. β.*

As very slight contaminations may impair the distinctness of the tints exhibited by the precipitates considered at § 110. 3. *b. β.*, it is advisable, in all cases where the slightest contamination is suspected, to adopt the following method for the detection of manganese, chromium, zinc, and alumina.

Potass in excess is added to a portion of the original solution.

aa. A whitish precipitate is formed, which does not redissolve in an excess of the precipitant, and changes its color speedily to a blackish-brown when exposed to the air: MANGANESE. The blow-pipe is resorted to as a conclusive test. (§ 89. *b.*)

bb. A precipitate is formed which redissolves in an excess of the precipitant: OXIDE OF CHROMIUM, ALUMINA, ZINC.

αα. Sulphuretted hydrogen water is added to a portion of the potass solution. The formation of a white precipitate indicates the presence of ZINC.

ββ. If the original solution, or the potass solution is green, and the precipitate, produced by potass and subsequently redissolved in the excess of the precipitant, was of a bluish color, OXIDE OF CHROMIUM is present. To remove all doubt on this point, the potass solution is heated to ebullition, or the blow-pipe resorted to. (§ 88. *b.*)

γγ. Chloride of ammonium is added to the potass solution. The formation of a white precipitate indicates the presence of ALUMINA. The test with solution of cobalt before the blow-pipe is conclusive. (§ 88. *a.*)

4. Chloride of ammonium and carbonate of ammonia, mixed with a small quantity of caustic ammonia, are added to a portion of the original solution, and heat applied.

a. NO PRECIPITATE IS FORMED: absence of barytes, strontia, and lime. Pass over to § 110. 5.

b. A PRECIPITATE IS FORMED. Presence of barytes, strontia, or lime.

Solution of gypsum is added to a portion of the original solution, and heat applied.

a. *The solution does not become turbid, even after the lapse of from five to ten minutes:* LIME. The test with oxalic acid is selected as a confirmatory proof. (§ 87. *c.*)

β. *The solution becomes turbid after the lapse of some time:* STRONTIA. The alcohol flame is resorted to as a conclusive test. (§ 87. *b.*)

γ. *A precipitate is immediately formed:* BARYTES. To remove all doubt on this point, test with hydrofluosilicic acid. (§ 87. *a.*)

5. Phosphate of soda is added to the solution of 4. *a.* (in which carbonate of ammonia has failed to produce a precipitate, after previous addition of chloride of ammonium.

a. NO PRECIPITATE IS FORMED, not even after agitating the solution: absence of magnesia. Pass over to § 110. 6.

b. A CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIA.

6. A drop of the original solution is evaporated on a platinum plate and the residue ignited.

a. NO FIXED RESIDUE REMAINS. Solution of potass is added to the original solution. The odor and reaction of the escaping gas, and the fumes which it forms with acetic acid, will prove the presence of AMMONIA. (§ 86. *c.*)

b. A FIXED RESIDUE REMAINS. Potass or soda. A portion of the original solution is mixed with tartaric acid and vigorously shaken. (Should the original solution be highly diluted, it will be necessary to comcentrate it in the first place, by evaporation.)

α. *No precipitate is formed, not even after the lapse of ten or fifteen minutes:* SODA. The blow-pipe flame and alcohol flame are selected as conclusive tests. (§ 86. *b.*)

β. *A crystalline granular precipitate is formed:* POTASS bichloride of platinum, the blow-pipe flame, and alcohol flame, are selected as conclusive tests. (§ 86. *a.*)

Compounds which are supposed to contain but one acid and one base, &c.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 111.

The analyst should in the first place reflect *which* of the inorganic acids form soluble compounds with the detected base, and to bear this carefully in mind in his subsequent operations.

1. I have already spoken of the detection of ARSENIOUS ACID and ARSENIC ACID while treating of the detection of the bases. These two acids are distinguished from each other by their respective deportment with nitrate of silver, or with potass and sulphate of copper. (§ 95. *d.* and *e.*)

2. While pursuing the systematic course for the detection of the bases, the operator is led to the detection of CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID. The two former betray their presence by effervescing upon the addition of hydrochloric acid; they may be distinguished from one another by their odor. Should additional proof be required, the presence of carbonic acid may be ascertained beyond doubt by the reaction with lime water (vide § 100. *a.*), and that of sulphuretted hydrogen by the reaction with solution of lead. (§ 101. *e.*) Chromic acid may be detected invariably by the yellow or red tint of the solution, and likewise by the transition of this red or yellow color to green, attended with separation of sulphur, upon the addition of sulphuretted hydrogen water. To remove all doubt on this point, the reactions with solution of acetate of lead and solution of nitrate of silver may be finally resorted to. (§ 97. *b.*)

3. Chloride of barium is added to a portion of the solution, which, should its reaction be acid, is to be neutralized first, or rendered feebly alkaline, by addition of ammonia.

a. THE FLUID REMAINS CLEAR. (Pass over to § 111. 4.) The absence of sulphuric acid, phosphoric acid, and silicic acid is certain, that of oxalic acid and boracic acid probable. The barytes compounds of the two latter acids are kept in solution by ammoniacal salts, and borate of barytes, moreover, does not separate from *dilute* solutions, even though no ammoniacal salts be present.

b. A PRECIPITATE IS FORMED. Dilute hydrochloric acid is added in excess.

α. *The precipitate dissolves.* Absence of sulphuric acid. Pass over to 4.

β. *The precipitate remains undissolved,* even though a copious quantity of water be added : SULPHURIC ACID.

4. Solution of gypsum is added. A portion of the original solution (which, should it have an acid reaction, is likewise first to be rendered neutral or feebly alkaline, by the addition of ammonia) ; should no ammoniacal salt be present, the addition of the solution of gypsum is to be preceded by that of some sal ammoniac.

a. NO PRECIPITATE IS FORMED : absence of oxalic acid and phosphoric acid. Pass over to § 111. 5.

b. A PRECIPITATE IS FORMED. Acetic acid is added in excess.

α. *The precipitate is redissolved* : PHOSPHORIC ACID. The reactions with sulphate of magnesia in conjunction with ammonia, with solution of nitrate of silver, and before the blow-pipe, are employed as conclusive tests. (§ 99, *a.*)

β. *The precipitate remains undissolved,* but dissolves readily in hydrochloric acid : OXALIC ACID. The reaction with concentrated sulphuric acid is selected as a conclusive test. (§ 99. *c.*)

5. A fresh portion of the original solution is acidified with nitric acid, and solution of nitrate of silver is subsequently added.

a. THE FLUID REMAINS CLEAR. This is a certain indication of the absence of chlorine and iodine. The absence of cyanogen is also probable. (Of the soluble metallic cyanides, percyanide of mercury is not precipitated by nitrate of silver; and from the nature of the detected base, the operator may judge whether he ought to take the possible or probable presence of the substance into account or not; for the manner in which the detection of the cyanogen in the percyanide of mercury, is effected, I refer to § 101. *d.*) Pass over to § 111. 6.

b. A PRECIPITATE IS FORMED. Ammonia is added in excess.

α. *The precipitate does not dissolve:* IODINE. As a conclusive test we select the reaction with starch. (§ 101. *c.*)

β. *The precipitate redissolves.* If it redissolves readily, there is reason to suppose that CHLORINE is present; if it dissolves with difficulty and only upon the addition of a large portion of ammonia, CYANOGEN may be supposed to be present. The presence of chlorine may be ascertained beyond doubt, by testing the original solution with protonitrate of mercury, and from the deportment of the silver precipitate at a high temperature. (§ 101. *a.*) The presence of cyanogen may be ascertained positively by adding potass, solution of ferroso-ferric oxide and hydrochloric acid to the original solution. (§ 101. *d.*)

6. A portion of the solid substance—(or, should the body to be examined exist in the fluid state, *the residue remaining after evaporation*)—is drenched with some sulphuric acid; alcohol is then added and subsequently kindled. Should the flame appear green, upon stirring, this is a proof of the presence of BORACIC ACID.

7. With regard to the presence of nitric acid, this is usually discovered already in the course of the preliminary examination, (vide § 107. 1. 2. *c.*) To ascertain the presence of this acid beyond doubt, the reaction with protosulphate of iron and sulphuric acid, or that with solution of indigo, are resorted to. (§ 102. *a.*)

8. I refer to § 126 for the detection of chloric acid, hydrofluoric acid, silicic acid, and bromine.

Compounds which are supposed to contain only one acid and one base, &c.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

II. *Detection of organic acids.*

§ 112.

1. To a portion of the aqueous solution of the compound under examination, ammonia is added to feeble alkaline reaction, and subsequently chloride of calcium. Should the solution be neutral the addition of the chloride of calcium is to be preceded by that of some chloride of ammonium.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER AGITATING THE SOLUTION, NOR AFTER THE LAPSE OF A FEW MINUTES: absence of oxalic acid and tartaric acid. Pass over to § 112. 2.

b. A PRECIPITATE IS FORMED. Lime-water is added in excess to a portion of the original solution, and the precipitate formed is acted upon with solution of sal ammoniac.

α. *The precipitate redissolves:* TARTARIC ACID. The reaction with acetate of potass may be resorted to as a confirmatory test; but a still more positive proof will be afforded by the deportment which the precipitate produced by the chloride of calcium exhibits with caustic potass. (§ 103. *b.*)

β. *The precipitate does not redissolve :* OXALIC ACID. The reaction of concentrated sulphuric acid is selected as a conclusive test. (§ 99 *c.*)

2. The fluid of 1. *a.* is heated to boiling, and for some time maintained in a state of ebullition; some more ammonia is finally added to the boiling fluid.

a. IT REMAINS PERFECTLY TRANSPARENT: absence of citric acid. Pass over to § 112. 3.

b. IT BECOMES TURBID, AND DEPOSITS A PRECIPITATE: CITRIC ACID.

3. The fluid of 2. *a.* is mixed with alcohol.

a. IT REMAINS PERFECTLY TRANSPARENT: absence of malic acid. Pass over to § 112. 4.

b. A PRECIPITATE IS FORMED: MALIC ACID. To remove all doubt on this point, it is *invariably* necessary to have recourse to the reaction with acetate of lead. (§ 103. *e.*)

4. A portion of the original solution is neutralized *perfectly* (if not already absolutely neutral) either with ammonia or with hydrochloric acid, and solution of perchloride of iron is subsequently added.

a. A BULKY PRECIPITATE FORMS OF A CINNAMON OR DIRTY YELLOW COLOR. The precipitate is washed and subsequently heated with ammonia; the solution is filtered and the filtrate concentrated by evaporation; it is then divided into two portions, and some hydrochloric acid added to the one: the formation of a precipitate indicates BENZOIC ACID. The other portion is mixed with alcohol and chloride of barium added: the formation of a precipitate indicates SUCCINIC ACID. (Compare § 104. *a.* and *b.*)

b. THE LIQUID ACQUIRES A TOLERABLY INTENSE DEEP RED TINT, AND, UPON PROTRACTED BOILING, A LIGHT REDDISH-BROWN PRECIPITATE SEPARATES: acetic acid or formic acid. A portion of the solid salt under examination, or, should the substance to be analysed happen to be in the fluid state, of the residue remaining upon the evaporation of the liquid—(which, if acid, is first to be neutralized with potass)—is heated with sulphuric acid and alcohol, (§ 105. *a.*) The characteristic odor of acetic ether. indicates the presence of ACETIC ACID.

If the operator fail to detect acetic acid in the fluid, he may conclude that the substance under examination contains

FORMIC ACID: all doubt on this point may be removed by the reactions with nitrate of silver and perchloride of mercury. (§ 105. *b.*)

Compounds which are supposed to consist of but one acid and one base, &c.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

*Detection of the base.**

§ 113.

A portion of the solution in hydrochloric acid, nitric acid, or aqua regia, is diluted with water,† and the further operations are conducted exactly as directed at § 110, beginning at 1. in cases where the substance is dissolved in nitric acid, and at 2. if the solution contains already hydrochloric acid. I must claim particular attention of the student to the following remark. I have stated at § 110. 3. *b.* *β.* *cc.* that, if in cases where we have A SUBSTANCE SOLUBLE IN WATER before us, we obtain, in the course of the examination, a white precipitate upon testing with hydrosulphuret of ammonia—(after having neutralized with ammonia the free acid either originally present in or previously added to the solution under examination)—this precipitate can consist only either of sulphuret of zinc, or of alumina. But the case is different when the substance is INSOLUBLE IN WATER, but dissolves in hydrochloric acid; for in that case a white precipitate produced by hydrosulphuret of ammonia, in the presence of sal ammoniac, may consist also of a PHOSPHATE OF THE ALKALINE EARTHS, and likewise of OXALATE OF LIME, BARYTES, and STRON-

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* Regard has here been had likewise to certain salts, since this course of examination leads directly to their detection.

† If upon the addition of the water, the liquid becomes turbid or deposits a white precipitate, this indicates the presence of antimony, bismuth, or tin. (Compare § 108. 4.

TIAN. If, therefore, a white precipitate is produced upon testing an acid solution, under the circumstances stated, and according to the directions of § 110. 3. *b.* *β.* *cc*, the following method is to be pursued. Caustic potass in excess is added to a small portion of the original hydrochloric solution.

1. THE PRECIPITATE WHICH FORMS AT FIRST, REDISSOLVES IN AN EXCESS OF THE PRECIPITANT; absence of the salts of the alkaline earths; presence of ZINC or ALUMINA; to distinguish between these, the potass solution is tested with sulphuretted hydrogen and chloride of ammonium. (Vide supra § 110. 3. *b.* *β.* *cc.*) The alumina may have been present and precipitated as PHOSPHATE OF ALUMINA. This is ascertained by dissolving the precipitate in hydrochloric acid, adding tartaric acid, supersaturating with ammonia and mixing with sulphate of magnesia. If phosphoric acid is really present, a precipitate of basic phosphate of ammonia and magnesia will form upon the joint addition of these reagents, (in most cases however only after the lapse of some time.)

2. THE PRECIPITATE FORMED DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT. Presence of a phosphate or oxalate with an alkaline earthy base. It is now, in the first place, necessary to ascertain by preliminary examination, whether we have an oxalate or a phosphate before us; for this purpose a portion of the original substance under examination is ignited. Should it be converted into a carbonate by this process, either with slight, or without any nigrescence, the salt under examination is an OXALATE, whilst if it remains unaltered upon ignition, this is a sure proof that we have a PHOSPHATE before us. Whether the ignited compound has been transformed into a carbonate, is readily ascertained by pouring some water over the ignited mass and treating it subsequently with acids, when ensuing effervescence will set the matter at once at rest, (the examined salt not presenting this property previously to its ignition.)

a. THIS PRELIMINARY EXAMINATION DENOTED THE PRESENCE OF A PHOSPHATE.

To a portion of the original hydrochloric solution, ammonia is added to feebly alkaline reaction, and subsequently acetic acid until the precipitate formed is redissolved; a drop of solution of perchloride of iron is then added. The ensuing formation of a yellowish-white gelatinous precipitate (perphosphate of iron) confirms the presence of PHOSPHORIC ACID. Solution of perchloride of iron is now dropped into the same fluid until the latter appears distinctly red (owing to the formation of peracetate of iron; the mixture is then heated to boiling and maintained for some time in a state of ebullition, whereupon a ruddy brown precipitate will separate, which is then to be filtered off from the colorless fluid immediately after the ebullition has ceased. By this operation the phosphoric acid is separated from its basis and precipitated in combination with peroxide of iron, and in conjunction with free hydrated peroxide of iron, whilst the filtrate contains the alkaline earthy base in combination with chlorine; the precise nature of this base is finally ascertained in the usual manner. (Vide 110. 4.)

b. THE PRELIMINARY EXAMINATION INDICATED THE PRESENCE OF AN OXALATE.

Two ways are open in this case to ascertain beyond doubt the nature of the acid and base:—

1. A portion of the compound under examination is ignited, the residue subsequently dissolved in hydrochloric acid, and the solution finally tested in the usual manner for the alkaline earthy base. Another portion of the substance under examination is then tested with concentrated sulphuric acid, to remove all doubt as to the presence of oxalic acid. (§ 99. *c.*)

2. A portion of the compound is boiled for some time with a concentrated solution of carbonate of potass, and the fluid subsequently filtered off from the residue. This residue contains the alkaline earth, (which forms the base of the substance under examination,) in combination with carbonic acid, whilst the filtrate contains the oxalic acid

in combination with potsss. The filtrate is now acidified with acetic acid, and the presence of the oxalic acid is then finally proved by testing with solution of gypsum. (§ 99. *c.*) The residue is thoroughly washed, subsequently dissolved in hydrochloric acid, and the solution treated in the usual manner—vide § 110. 4.

Compounds which are supposed to consist of but one acid and one base, &c.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 114.

1. CHLORIC ACID cannot be present, since all chlorates without exception are soluble in water; the nitrates also, with the exception of a few, being soluble in water, the presence of NITRIC ACID may usually be disregarded. The basic nitrate of bismuth forms the most frequently occurring exception to the general rule of the solubility of the nitrates in water. The presence of nitric acid in *insoluble* nitrates may be most readily recognized by the deflagration which ensues upon throwing a sample of the compound under examination upon red-hot charcoal. The deflagration which ensues upon fusing a nitrate in conjunction with cyanide of potassium, is a still more conclusive test. (Vide § 102. *a.*) For the analysis of those of the metallic cyanides which are insoluble in water, I refer to § 131.

2. The course of examination which I have laid down for the detection of the bases leads likewise to that of ARSENIOUS and ARSENIC ACID, CARBONIC ACID, HYDROSULPHURIC ACID, and

CHROMIC ACID. With regard to the latter acid, I repeat here that its presence is indicated by the yellow or red color of the compound, the evolution of chlorine which ensues upon boiling with hydrochloric acid, and the subsequent discovery of oxide of chromium in the solution. Fusion of the compound under examination with carbonate of soda and nitrate of potass, however, is the most conclusive test for chromic acid. (§ 97. *b.*)

3. A sample of the substance under examination is boiled with nitric acid.

   a. If nitric oxide gas is evolved,—which may be readily recognized by the red fumes of nitrous acid forming in the air,—this indicates the presence of a SULPHURET; whilst the evolution of carbonic acid is indicative of a CARBONATE. The positive proof of the presence of a sulphuret may be obtained by testing the nitric solution with chloride of barium, with which reagent it must yield a precipitate of sulphate of barytes, which even a large proportion of water fails to dissolve. The blow-pipe also may be resorted to as a conclusive test for sulphurets. (Vide § 101. *a.*)

   b. If violet vapors escape, the compound may be supposed to be an IODIDE. A slip of paper, covered with moist starch, forms the most conclusive test for iodine. (§ 101. *c.*)

4. A portion of the nitric acid solution (which is to be filtered first, should the acid have failed to dissolve the whole of the sample) is diluted with water, and tested subsequently with nitrate of silver. The formation of a white precipitate, soluble in ammonia, and fusing without decomposition when heated, is indicative of the presence of CHLORINE.

5. A sample of the substance is boiled with hydrochloric acid, and the solution subsequently filtered, should the acid fail to dissolve the whole of the sample. The solution or filtrate, as the case may be, is then diluted with water, and nitrate of barytes added. The formation of a white precipitate, which does not redissolve, even though a copious amount of water be added to the

fluid from which it has separated, indicates the presence of SULPHURIC ACID.

6. Test for BORACIC ACID as directed at § 111.

7. Should none of these acids be present, the analyst may suspect the presence of either PHOSPHORIC ACID or OXALIC ACID, or the absence of all acids. Were the phosphoric acid combined with an alkaline earth, and the oxalic acid with lime, barytes, or strontia, they would have been detected already while testing for these bases. (§ 113.) The presence of these two acids, accordingly, is to be suspected only if the examination for bases has revealed the presence of other bases than the alkaline earths. Should this be the case, the fluid is prepared for further examination by precipitating and separating the heavy metals from it—(this is effected in acid solutions by means of sulphuretted hydrogen, and in alkaline solutions by hydrosulphuret of ammonia)—and is then subsequently tested for phosphoric acid and oxalic acid, according to the instructions given at § 111. 4.

8. For the detection of SILICIC ACID, BROMINE, and FLUORINE, I refer to § 126, (at the end).

Compounds which are supposed to consist of but one base and one acid, &c.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

DETECTION OF THE ACID.

II. *Detection of organic acids.*

§ 115.

1. A sample of the substance under examination is dissolved in the smallest possible quantity of hydrochloric acid. If a residue remains, this must be filtered off, and subsequently tested for BENZOIC ACID by heating it. Carbonate of potass in excess

is added to the solution or filtrate, (as the case may be,) and the mixture is boiled for some time, and subsequently filtered. The alkaline filtrate which contains the organic acid, under all circumstances, is exactly saturated with hydrochloric acid, and the mixture subsequently tested, as directed § 112. No regard need be had to formic acid, all the formiates being soluble in water.

2. Acetic acid is most readily detected in such compounds by means of sulphuric acid and alcohol. (§ 105. *a.*)

Compounds which are supposed to consist of but one acid and one base, &c.

C. Substances insoluble or sparingly soluble in water, hydrochloric acid, nitric acid, or aqua regia.

DETECTION OF THE BASE AND THE ACID.

§ 116.

Under this head we have to consider here sulphate of barytes, sulphate of strontia, sulphate of lime, silica, sulphate of lead, chloride of lead, and chloride of silver, as the most frequently occurring compounds belonging to this class. For the less frequently occurring insoluble compounds, I refer to § 130.

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are, at all events, of very difficult solution, I have included them among the class of insoluble substances, that they may be detected here, should they have escaped detection in the course of the examination of the aqueous or acid solutions of the substances to be analyzed.

1. A very minute quantity of the substance under examination is treated with hydrosulphuret of ammonia.

a. It becomes black; this indicates the presence of a salt of lead or of chloride of silver. A somewhat larger portion of the substance is then digested for some time with hydrosulphuret of ammonia. This effects the decomposition of the metallic salt and the formation of a sulphuret, which latter remains undissolved, whilst we have in solution the acid of the metallic salt combined with the ammonia of the hydrosulphuret of ammonia. The solution is filtered off from the undissolved sulphuret, which is then washed, and subsequently dissolved in nitric acid, the solution being afterwards tested for lead, with sulphuric acid; and for silver, with hydrochloric acid, aided by the subsequent addition of ammonia. One portion of the filtrate is tested for sulphuric acid, with chloride of barium, after having previously decomposed the excess of the hydrosulphuret of ammonia, by adding hydrochloric acid and boiling the mixture; another portion is tested for hydrochloric acid, with solution of nitrate of silver, after previous acidification of the liquid with nitric acid, and ebullition of the mixture.

b. It remains white. Absence of a heavy metallic oxide. A small portion of the very finely levigated substance under examination is mixed with four times its quantity of carbonate of soda and potass, and the mixture is introduced into a small platinum crucible, and fused over a Berzelius' spirit-lamp. The fused mass is boiled with water.

a. *Complete solution ensues:* silica. All doubt regarding the presence of this substance may be removed by supersaturating the solution with hydrochloric acid, and evaporating to dryness. This operation serves to convert the silicic acid into the insoluble modification. It will, accordingly, now remain undissolved upon treating the residue with water. If the residue be mixed with carbonate of soda, and exposed to a strong blow-pipe flame, a clear button will be produced. (§ 100. *b*.)

β. *A white residue remains;* this indicates the presence of a SULPHATE OF THE ALKALINE EARTHS. The solution is filtered, the filtrate acidified with hydrochloric acid and diluted with water, the fluid then tested for SULPHURIC ACID, with chloride of barium. The white residue (which contains the alkaline earth in form of a carbonate) is carefully washed, dissolved in a small quantity of dilute hydrochloric acid, and the solution tested for BARYTES, STRONTIA, and LIME, according to the instructions given at § 110. 4.

Compounds in which all the more frequently occurring Bases, Acids, Metals, and Metalloids, are supposed to be present.

A. SUBSTANCES BOTH SOLUBLE AND INSOLUBLE IN WATER, AND SOLUBLE IN HYDROCHLORIC ACID OR NITRIC ACID.

Detection of the bases.[*]

§ 117.

I have taken classes I. and II. (vide § 109.) together here, because the systematic course, and method of examination is in most cases the same for both classes. Those parts which refer only to substances insoluble in water, but soluble in hydrochloric acid or nitric acid, are enclosed between inverted commas (" ——"), and may therefore be passed over unnoticed, when examining substances, soluble in water.

I. SOLUTIONS IN WATER.

A small quantity of hydrochloric acid is added.

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION PREVIOUSLY TO THE ADDITION OF THE HYDROCHLORIC ACID.

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[*] The arsenious and arsenic acid, and several salts, are also included here, since this course of examination leads to their detection.

a. NO PRECIPITATE IS FORMED: this indicates the absence of silver and protoxide of mercury. Pass over to § 118.

b. A PRECIPITATE IS FORMED; hydrochloric acid is added to the solution drop by drop, until the quantity of the precipitate ceases to increase; about six or eight drops more of hydrochloric acid are then added, the mixture shaken, and the fluid subsequently filtered off from the precipitate. (The precipitate produced by the hydrochloric acid may consist of chloride of silver, protochloride of mercury, chloride of lead, a basic salt of antimony, or possibly also of benzoic acid. The basic salt of antimony, however, redissolves in the excess of the hydrochloric acid; consequently if the instructions given here have been strictly followed, the precipitate collected upon the filter can consist only of chloride of silver, protochloride of mercury, and chloride of lead, — with benzoic acid, we have no business in this place.)

The precipitate collected upon the filter is washed twice with water, and the rinsings are added to the filtrate, the latter is then examined strictly according to the directions of § 118, even though the addition of the rinsings to the acid filtrate should produce turbidity in the fluid; (this indicates the presence of compounds of antimony, bismuth, or protoxide of tin)

The washed precipitate is now treated as follows:

α. Hot water is poured over the twice-washed precipitate upon the filter, and the fluid running off is tested for LEAD, with sulphuric acid. (The non-formation of a precipitate, upon the addition of the sulphuric acid, proves simply that the precipitate produced by hydrochloric acid contains no lead, but not by any means the total absence of lead, since hydrochloric acid fails to precipitate very dilute solutions of lead.)

β. Solution of ammonia is poured over the well washed precipitate upon the filter. Should the precipitate upon this turn black or grey, this is a sign of the presence of PROTOXIDE OF MERCURY.

γ. The ammoniacal fluid running off in β., is mixed with nitric acid. The formation of a white, curdy precipitate indicates the presence of SILVER. (Should the precipitate contain lead, the ammoniacal solution will generally appear turbid, owing to the separation of a basic salt of lead.)

This, however, does not interfere with the testing for silver, since the basic salt of lead redissolves upon the addition of nitric acid.

2. THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION.

a. THE ADDITION OF HYDROCHLORIC ACID TO STRONGLY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON CONTINUED ADDITION OF HYDROCHLORIC ACID; pass over to § 118. With regard to the passages between inverted commas, and which relate to substances insoluble in water, the analyst has to look simply to that referring to phosphate of alumina; should an ammoniacal salt be present, however, likewise to that referring to the oxalates of the alkaline earths, (with the exception of oxalate of lime,) since the solution of these compounds in a fluid with alkaline reaction is not impossible.

b. THE ADDITION OF HYDROCHLORIC ACID TO THE ORIGINAL SOLUTION PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, NOT EVEN UPON BOILING.

α. *The formation of the precipitate is not attended with evolution of sulphuretted hydrogen nor of hydrocyanic acid.* The fluid is filtered off from the precipitate, and the filtrate treated according to § 118.

aa. THE PRECIPITATE IS WHITE. It can, in that case, consist only of CHLORIDE OF LEAD, SULPHATE OF LEAD, OR CHLORIDE OF SILVER. Test for the bases and acids of these three compounds according to the instructions of § 130, bearing in mind that the chloride of lead or chloride of silver which may happen to be found may have been formed in the process.

bb. THE PRECIPITATE IS YELLOW OR ORANGE. In this case it may consist of SULPHURET OF ARSENIC, (or if the fluid from which it separated was not boiled long, or with very dilute hydrochloric acid only, also of sulphuret of antimony or bisulphuret of tin,) which substances were originally dissolved in solution of ammonia, borax, phosphate of soda, or some other alkaline fluid, with the exception of solutions of alkaline sulphurets and cyanides. The precipitate is tested according to § 119.

*β. The formation of the precipitate is attended with evolution of sulphuretted hydrogen gas, but not of hydrocyanic acid.**

aa. THE PRECIPITATE IS OF A PURE WHITE COLOR, AND CONSISTS OF SEPARATED SULPHUR. In this case an alkaline sulphuret with excess of sulphur is present. Filter the solution and pass over to § 121, bearing in mind that of the substances considered in that paragraph alumina and oxide of chromium alone can be present.

bb. THE PRECIPITATE IS COLORED. In this case we may conclude that a metallic sulphur salt is present, i. e. a combination of an alkaline sulphur base with an electro-negative sulphuret. The fluid is filtered off from the precipitate, and the filtrate is treated as directed in *aa.* The precipitate is treated according to the directions given at § 118. 3. It may consist of SULPHURET OF

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* Should the odor of the evolved gas leave the analyst in doubt regarding the actual presence or absence of hydrocyanic acid, he need simply add some chromate of potass to a sample of the fluid, previously to the addition of the hydrochloric acid.

GOLD, SULPHURET OF PLATINUM, SULPHURET OF TIN, SULPHURET OF ARSENIC, OR SULPHURET OF ANTIMONY. It might, however, consist also of BISULPHURET OF MERCURY or of SULPHURET OF COPPER, or contain either of these substances, since the former is readily soluble in sulphuret of potassium, and the latter slightly soluble in sulphuret of ammonium.

γ. *The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of sulphuretted hydrogen.* This indicates the presence of an ALKALINE CYANIDE, and, if the evolution of the hydrocyanic acid is attended with that of sulphuretted hydrogen, likewise of an alkaline SULPHURET, in this case the precipitates may, besides the compounds enumerated sub. α. and β., contain many other substances, (e. g. sulphuret of nickel, cyanide of nickel, cyanide of silver, &c.) The mixture is kept boiling (with further addition of hydrochloric acid) until the whole of the hydrocyanic acid is expelled; the solution, or, should any undissolved residue remain, the filtrate is treated according to § 118, the residue (if any remain) is treated according to § 130.

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS.

α. *The escaping gas smells of sulphuretted hydrogen;* this indicates a SIMPLE ALKALINE SULPHUR COMPOUND. The further operations are conducted as directed at *b. β. aa.*

β. *The escaping gas is inodorous;* in this case it is carbonic acid which was combined with an alkali. Pass over to § 118.

γ. *The escaping gas smells of hydrocyanic acid* (no matter whether sulphuretted hydrogen or carbonic acid are evolved likewise or not). This indicates the presence of an ALKALINE CYANIDE. The mixture is kept boiling until the whole of the hydrocyanic acid is expelled, and is then treated according to the instructions which will be found at § 118.

II. SOLUTIONS IN HYDROCHLORIC ACID.

These are treated as § 118. directs.

III. SOLUTIONS IN NITRIC ACID

A small portion of the solution is diluted with much water.

1. IT REMAINS TRANSPARENT: add hydrochloric acid.

a. No precipitate is formed. Absence of silver. The original solution is treated according to § 118.

b. A precipitate is formed. If this does not redissolve upon heating the fluid, but is subsequently, when thoroughly washed, dissolved by ammonia, SILVER is present. The original solution is treated as directed at § 118.

2. THE SOLUTION BECOMES MILKY: BISMUTH OR ANTIMONY. The fluid is filtered, and the filtrate tested for silver according to the directions of § 117. III. 1.; the original solution is treated as § 118 directs.

§ 118.

SOLUTION OF SULPHURETTED HYDROGEN IS ADDED TO A SMALL PORTION OF THE CLEAR ACID SOLUTION, UNTIL THE FLUID, WHEN AGITATED, EMITS A CLEARLY PERCEPTIBLE ODOR OF SULPHURETTED HYDROGEN; HEAT IS THEN APPLIED.

a. NO PRECIPITATE IS FORMED, not even after the lapse of some time. Pass over to § 121, for neither lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, nor arsenic,* are present;† the absence of peroxide of iron and of chromic acid is also indicated by this negative reaction.

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* Should the preliminary examination have led the analyst to suspect the presence of arsenic acid, he ought to endeavour now to obtain the most conclusive evidence of the absence of this acid; this may be effected by allowing

b. A PRECIPITATE IS FORMED.

aa. The precipitate is of a pure white color, slight and pulverulent, and does not redissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of PEROXIDE OF IRON.‡ None of the other metals, enumerated at § 118. *a.* can be present. The original solution is treated as § 121 directs.

bb.. The precipitate is colored.

Solution of sulphuretted hydrogen is added to the larger portion of the acid or acidified solution, until the latter smells distinctly of sulphuretted hydrogen, and the precipitate ceases to increase upon contiuued addition of the reagent; the mixture is then heated nearly to boiling, and strongly agitated for some time.

In many cases, and more particularly when there is any reason to suspect the presence of arsenic, it will be found more to the purpose, to transmit sulphuretted hydrogen gas through the diluted solution, instead of adding sulphuretted hydrogen water.

1. THE PRECIPITATE IS OF A PURE YELLOW COLOR. In this case it can consist only of ARSENIOUS or ARSENIC ACID, of PEROXIDE OF TIN, or of OXIDE OF CADMIUM. The fluid—(which is

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the sample to stand at rest for some time, or by adding sulphurous acid to it previously to the addition of the sulphuretted hydrogen. (Compare § 95. *e.*)

† In solutions containing much free acid, the precipitates are frequently formed only after dilution with water.

‡ Sulphur will precipitate also if sulphurous acid, iodic acid, bromic acid, are present, (these substances do not come within the scope of the present work,) and also if chromic acid, chloric acid, or free chlorine are present. In presence of chromic acid, the separation of the sulphur is attended with reduction of the acid to oxide of chromium, in consequence of which the reddish-yellow color of the solution changes to green. (Compare § 97. *b.* 3.) The white sulphur suspended in the solution, appears at first like a green precipitate, which frequently tends to mislead novices.

subsequently to be tested according to § 121)—is separated from the precipitate,* and the latter washed, and a small portion of it digested with ammonia.

a. The precipitate is completely redissolved: absence of cadmium. The rest of the precipitate is tested for TIN and ARSENIC, according to the directions of § 119. 1.

b. A yellow residue remains even after addition of a further amount of ammonia and application of a moderate heat; CADMIUM. The whole of the precipitate is treated like the sample, and the fluid is subsequently filtered off from the undissolved residue; hydrochloric acid in excess is added to the filtrate. The non-formation of a precipitate denotes that the first precipitate consisted exclusively of sulphuret of cadmium; but if a precipitate is formed, this may consist of PEROXIDE OF TIN, or ARSENIC, and is to be examined according to § 119. 1.

2. THE PRECIPITATE IS ORANGE RED, OR YELLOW, WITH A SHADE OF ORANGE It indicates ANTIMONY, but may, moreover, contain TIN—(should this metal have been present as peroxide)—ARSENIC or CADMIUM; the precipitate is separated from the fluid —(which is subsequently tested as § 121 directs)—washed, and a small portion of it digested with hydrosulphuret of ammonia containing an excess of sulphur.

a. It redissolves completely: absence of cadmium. The rest of the precipitate is treated as directed at § 119. 2.

b. A yellow residue remains, even after protracted digestion, with a larger quantity of hydrosulphuret of ammonia: CADMIUM. The entire precipitate is then treated in the same manner as the sample, and the fluid is subsequently filtered off from the sulphuret of cadmium; a slight excess of hydrochloric acid is added to the filtrate, and the precipitate formed is treated as directed at § 119. 2.

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* The best way of separating a precipitate from a fluid, and which ought to be pursued in qualitative analysis, whenever practicable, is to allow the precipitate to subside. This may almost invariably be effected by the application of heat and a vigorous shake of the fluid)—and to transfer the fluid alone to the filter, leaving the precipitate in the test cylinder, where it may subsequently be washed by decantation.

3. THE PRECIPITATE IS OF A DARK BROWN OR BLACK COLOR. The precipitate is separated from the fluid—(which is subsequently tested according to the directions of § 121)—washed with water, and a small portion of it is subsequently digested for some time, with hydrosulphuret of ammonia, containing an excess of sulphur.*

a. The precipitate redissolves completely in hydrosulphuret of ammonia (or sulphuret of potassium;) absence of cadmium, lead, bismuth, copper, and mercury: § 120 may therefore be passed over. The rest of the original precipitate is treated according to the instructions of § 119.

b. The precipitate is not redissolved, or at least not completely. The mixture is diluted with from four to five parts of water, the fluid is then filtered off from the precipitate, and hydrochloric acid in excess subsequently added to the filtrate.

α. *The fluid turns milky, owing to the separation of sulphur.* Absence of gold, platinum, tin, antimony, and arsenic. The rest of the original precipitate is treated according to the directions of § 120.

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* If the solution contains copper, which is generally revealed by the color of the fluid, and may be ascertained positively by testing with a clean iron rod, (vide § 92. *b*. 8.) solution of sulphuret of potassium is to be substituted for hydrosulphuret of ammonia, and the mixture is boiled, (vide § 92. *b*. 3.) But if the fluid, besides copper, contains likewise peroxide of mercury (the presence of which is generally sufficiently revealed by the several changes of color exhibited by the precipitate forming upon the addition of the sulphuretted hydrogen, (§ 92. *a*. 3.) and which, in donbtful cases, may be ascertained by testing a sample of the original acidified solution, with protochloride of tin,) hydrosulphuret of ammonia must be used, although the separation of the sulphuret of the antimony group from the sulphuret of copper is not fully effected in such cases; since were sulphuret of potassium used, the bisulphuret of mercury would dissolve in this reagent, and this would impede the further examination of the sulphurets of the antimony goup.

β. A colored precipitate is formed. The color of the precipitate is minutely inspected; the rest of the original precipitate is then treated like the sample, i. e. digested with hydrosulphuret of ammonia containing an excess of sulphur, or with sulphuret of potassium, as the case may be; the undissolved residue is allowed to subside, and the supernatant fluid is passed through the filter; the residue in the test-cylinder is once more digested with hydrosulphuret of ammonia (respect. sulphuret of potassium), and the fluid subsequently filtered off from the residue,* which latter is then washed and kept for further examination, according to the direction of § 120. The whole of the filtrate is diluted with some water, and a slight excess of hydrochloric acid added to the fluid; the mixture is now heated and the precipitate produced is treated as follows: (§ 119.)

§ 119.

THE PRECIPITATE PRODUCED BY HYDROCHLORIC ACID (§ 118. 3. *b.* γ.) IS:

1. OF A PURE YELLOW COLOR WITHOUT THE SLIGHTEST SHADE OF ORANGE: ARSENIC OF TIN. The fluid is filtered off from the precipitate, which is then thoroughly washed; a small portion of the washed precipitate is subsequently heated upon the lid of a porcelain crucible, or upon a broken piece of porcelain or glass.

a. Complete volatilization ensues: absence of tin. The rest of the precipitate is carefully dried and subsequently mixed with about six times its weight of a perfectly dry mixture of equal parts of carbonate of soda and cyanide of potassium; the whole mass is introduced into a small glass tube expanded into a bulb at one end; the heat of a BERZELIUS lamp is then applied. The formation of a metallic mirror is a positive proof of the presence of ARSENIC. Should the amount of the precipitate be very minute, the reduction is to be effected in a slow stream of carbonic acid gas (compare § 95. *d.* 10). Whether the arsenic was present in the form of arsenious acid or in that of arsenic acid, the analyst may ascertain by the method described at the end of § 95.

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* Should the residue readily subside, it is to be left in the test-cylinder, and washed by decantation. But if its subsidence proceeds slowly and with difficulty, it is to be transferred to and washed upon the filter; a hole is then made in the bottom of the filter, and the residue is washed with the aid of a syringe bottle, into a small porcelain basin; the application of a gentle heat will now materially aid the subsidence of the residue, so that the separated water may soon be readily decanted.

b. A fixed residue remains. Probable presence of tin. The rest of the precipitate is thoroughly dried upon the filter, and mixed subsequently with one part of effloresced soda and one part of nitrate of potass; the mixture is projected in small portions into a small porcelain crucible containing two parts of nitrate of potass in a state of fusion.*

The fusing mass is poured upon a broken piece of porcelain, (to preserve the crucible,) and allowed to cool; when cold, it is reduced to powder, and digested with cold water; the fluid is filtered off from the white residue, (which will remain if tin is really present,) and the latter is thoroughly washed; the presence of tin is then finally demonstrated by reducing the washed residue before the blow-pipe in conjunction with cyanide of potassium and carbonate of soda, and rubbing the reduced mass in a small mortar, with some water; in this latter operation, it is necessary to press strongly upon the mass. (Vide § 95. *c.* 7.)

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* Should the amount of the precipitate be so minute that this operation cannot be conveniently performed, the dry filter, with the precipitate adhering to it, is to be cut into small fragments, which are then to be rubbed together with some carbonate of soda and nitrate of potass, the whole mass (the paper as well as the powder) being subsequently projected into the fusing nitrate of potass. It is preferable, however, in such cases, to procure a sufficiently large amount of the precipitate, or there will be but little hope of effecting the positive detection of the tin.

Whether the tin was present as PROTOXIDE, the analyst may ascertain by mixing a small sample of the original aqueous or hydrochloric solution, with a drop of nitric acid and some perchloride of gold. (§ 95. *b.* 6.)

The filtrate is divided into two portions, and highly dilute nitric acid is added cautiously to the one to feebly acid reaction, and heat applied.* Nitrate of silver is then added, and the fluid filtered; should any chloride of silver separate, (which will invariably happen in cases where the reagents were not perfectly pure, or the precipitate has not been thoroughly washed.) A layer of very dilute solution of ammonia (20 parts of water to one part of common ammonia) is gently poured upon the filtrate, the tube being held in an oblique position for this purpose, so that the solution of ammonia may run down the side; the mixture is then allowed to stand at rest for some time. The formation of a reddish-brown precipitate, which appears hovering cloud-like between the two layers, (and may be seen far more readily and distinctly by reflected than by transmitted light,) denotes the presence of ARSENIC. To gain more positive information on this point, the second portion of the filtrate (of the solution of the deflagrated mass) is precipitated with solution of neutral acetate of lead; the precipitate is filtered off, dried between blotting paper, and subsequently exposed on charcoal to the inner blow-pipe flame. If arsenic is really present, a globule of metallic lead containing an admixture of arsenic will be produced, which will emit the garlic odor of arsenic very long and continuously whenever exposed to the reducing blow-pipe flame. The only *positive proof* of the presence of arsenic, however, is the exhibition of this substance in the metallic state. (Compare § 95. *d.* and *e.*) Whether the arsenic was present in the form of arsenious acid, or in that of arsenic acid, the analyst may ascertain by the method described at the end of § 95.

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* In some cases where a rather larger proportion of carbonate of soda has been used, a trifling precipitate (hydrated peroxide of tin) will separate upon the acidification of the filtrate with nitric acid. This may be filtered off and tested for tin in the same manner as the undissolved residue, but if the presence of tin has been demonstrated already, this precipitate may be altogether disregarded, and the operation may at once proceed as directed above.

2. ORANGE-RED; OR YELLOW, WITH A SHADE OF ORANGE; ANTIMONY: TIN and ARSENIC may be present besides this metal. The precipitate is washed, dried, and subsequently deflagrated with nitre and carbonate of soda, in the same manner as directed at § 119. 1. *b.* The aqueous solution of the deflagrated mass is tested for ARSENIC, in strict conformity with the directions given in the same place.* The residue which remains upon treating the deflagrated mass with cold water, may be tested in three different ways.

a. The residue is thoroughly washed, mixed with cyanide of potassium and carbonate of soda, and the mixture is exposed, on charcoal, to the reducing flame of the blowpipe.

α. Metallic globules appear, which volatilize at last completely, with the emission of white fumes and the formation of a white crust. This demonstrates the presence of ANTIMONY, and the absence of tin.

β. Soft metallic globules remain, after long continued blowing: TIN.† The presence and nature of these globules may be ascertained best by rubbing the test specimen together with the surrounding particles of the charcoal in a mortar with some water. (§ 95. *c.*)

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* Should a precipitate (hydrated antimonic acid or hydrated peroxide of tin) form upon the acidification of the fluid filtered off from the residue remaining upon the extraction of the deflagrated mass with water, this may be filtered off and added to the residue. However, as the latter contains usually sufficient of tin and antimony, this precipitate may be altogether disregarded, and the process may at once proceed as directed at 119. 1. *b.*

† Whether the tin is present in the form of protoxide, may be ascertained in the same manner as directed at § 119. 1. *b.*

b. The residue is thoroughly washed with water, dried, and mixed with from four to five times its amount of cyanide of potassium; the mixture is introduced into a small porcelain crucible, fused by a strong heat and kept in fusion for some time. The fused mass is then cooled, and water subsequently poured over it; the mixture is heated to boiling, and the dross is thus separated from the metallic globules. These latter are treated with nitric acid, and the process for the detection of tin and antimony is conducted exactly as § 109. B. 2. *b.* directs.

c. The residue is thoroughly washed, and subsequently dissolved in hydrochloric acid; the solution is diluted, and a small zinc rod placed into it. When the action of the latter has ceased, and the reduction is complete, the reduced metals (which may be readily separated from the compact piece of zinc,) are boiled with nitric acid, and the further process is conducted exactly as § 109. B. 2. *b.* directs.

The two latter methods of detecting tin and antimony by the side of one another, are, for beginners at least, far safer than the first. But either of the three methods requires a sufficiently large amount of the precipitate.

3. BROWNISH-BLACK. GOLD OR PLATINUM; and, besides these, perhaps also ANTIMONY, ARSENIC, TIN. Add to the original solution of the substance.

a. Protochloride of tin; the formation of a reddish-brown or purple-colored precipitate denotes GOLD. The presence of this metal may be positively demonstrated by testing a portion of the original solution of the substance with protosulphate of iron, since this will effect the separation of metallic gold in the form of a black powder.

b. Chloride of ammonium; the formation of a yellow precipitate is indicative of the presence of PLATINUM. Should the solution be highly dilute, it is to be concentrated by evaporation, previously to the addition of the reagent.

A portion of the precipitate is tested for ARSENIC, as directed at § 119. 1. *a.* The rest is boiled with concentrated hydrochloric acid and the solution is subsequently filtered; the filtrate is tested for ANTIMONY by dropping one drop of it into water; (after having previously removed, as much as possible, the excess of acid by evaporation ;) if the water becomes milky, this denotes the presence of antimony. Or a small portion of the filtrate is mixed with solution of sulphuretted hydrogen; the formation of an orange-coloured precipitate indicates antimony. The rest of the hydrochloric solution is evaporated to dryness, and the residue mixed with carbonate of soda and cyanide of potassium ; the mixture is tested for PEROXIDE OF TIN, according to the directions of § 119. 2. Antimony and tin may, however, more safely be detected by precipitating them from the hydrochloric filtrate, by means of zinc, and conducting the further process strictly according to the directions of § 119. 2. *c.*

§ 120.

THE PRECIPITATE WHICH HAS NOT BEEN DISSOLVED BY HYDROSULPHURET OF AMMONIA, or sulphuret of potassium (§ 118. 3. *b.*) IS WASHED, AND SUBSEQUENTLY BOILED WITH NITRIC ACID. This operation is performed best in a small porcelain basin ; the boiling mass must be constantly stirred during the process.

1. THE PRECIPITATE DISSOLVES, AND NOTHING REMAINS FLOATING IN THE FLUID EXCEPT THE SEPARATED, LIGHT FLOCCULENT, YELLOW SULPHUR ; this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH, may be present. If the precipitate was originally of a pure yellow color, CADMIUM alone is present ; if it was originally brown or black, it is to be filtered off from the separated sulphur, and the filtrate is to be tested as follows :

a. Ammonia in excess is added to one third part of the filtrate.

a. No precipitate is formed: absence of lead and bismuth. Presence of COPPER, and perhaps also of cadmium.

(The presence of the copper is usually sufficiently demonstrated by the blue color of the ammoniacal fluid ; should it prove otherwise, however, the fluid is to be acidified with acetic acid and ferrocyanide of potassium added, when even the most minute traces of copper will be revealed by a light brownish red coloration and turbidity of the fluid.)

The rest of the filtrate is tested for *cadmium,* by adding carbonate of ammonia in excess, applying heat and allowing the mixture to stand at rest for some time. Should a white precipitate form, this consists of CADMIUM. Positive conviction on this point may be gained by dissolving this precipitate in hydrochloric acid adding sulphuretted hydrogen water to the solution, when the presence of cadmium will be positively demonstrated by the formation of a yellow precipitate.

β. A precipitate is formed : Presence of LEAD or BISMUTH, perhaps, also of copper and cadmium. The fluid is filtered off from the precipitate, and one half of the filtrate is tested for copper, (should the blue coloration of the ammoniacal fluid not sufficiently demonstrate the presence of this metal) ; the other half of the filtrate is slightly acidulated with hydrochloric acid, and tested for CADMIUM, with carbonate of ammonia in excess, as at *a.*

b. The rest of the nitric acid solution is divided into two parts, which are then respectively tested for lead and bismuth as follows :

a. A not too inconsiderable amount of dilute sulphuric acid is added to one part. The immediate or subsequent formation of a precipitate denotes the presence of LEAD. (In some instances the precipitate separates only after the lapse of a considerable time.) To render this reaction more distinct and marked, the greater part of the free nitric acid present, may be removed by evaporation, previously to the addition of the reagent.

β. The other part is evaporated to dryness and the residue treated with a few drops of water, and one or two drops of hydrochloric acid, according to its greater or less bulk. Heat is then applied, and the solution obtained is subsequently poured into a test cylinder filled with water. Ensuing turbidity demonstrates the presence of BISMUTH.*

2. THE BOILING NITRIC ACID FAILS TO REDISSOLVE THE WHOLE OF THE PRECIPITATED SULPHURETS, AND LEAVES AN UNDISSOLVED RESIDUE, BESIDES THE LIGHT FLAKES OF SULPHUR THAT FLOAT IN THE FLUID: Probable presence of PEROXIDE OF MERCURY, (the presence of this substance may be pronounced with almost positive certainty, if the precipitate is heavy and black.) The precipitate is allowed to subside, and the fluid is filtered off from it; the filtrate is to be tested for CADMIUM, COPPER, LEAD, and BISMUTH: a small portion of it is mixed with a copious amount of solution of sulphuretted hydrogen, and, should a precipitate form, the remainder is treated according to the directions of § 120. 1. The residue is washed, dissolved by the addition of a few drops of aqua regia, and ammonia added, until the solution retains only a feebly acid reaction; a drop of the fluid is then placed upon a clean copper plate. If MERCURY be present, the surface of the copper will, after the lapse of some time, exhibit a white stain, which presents a metallic lustre when rubbed, and disappears upon heating. Or the solution in aqua regia is evaporated nearly to dryness, some hydrochloric acid being added during evaporation; the residuary mass is diluted with some water, and protochloride of tin added. The formation of a preci-

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* For another method of distinguishing cadmium, copper, lead, and bismuth, from one another, I refer to Chapter II. (additions and remarks to §120.)

pitate, which appears white at first, but changes to grey upon the addition of an excess of protochloride of tin, is a positive proof of the presence of mercury.

§ 121.

A SAMPLE OF THE FLUID IN WHICH SOLUTION OF SULPHURETTED HYDROGEN HAS FAILED TO PRODUCE A PRECIPITATE, (§ 118. *a.*) OR OF THE FLUID WHICH HAS BEEN FILTERED OFF FROM THE PRECIPITATE FORMED, IS MIXED WITH AMMONIA TO ALKALINE REACTION, AND HYDROSULPHURET OF AMMONIA IS THEN ADDED, (no matter whether the ammonia has produced a precipitate or not.)

In cases where but a minute quantity of hydrochloric acid is present, and where, therefore, but little chloride of ammonium has been formed, a certain amount of solution of sal ammoniac is to be added to the fluid previously to the addition of the ammonia and hydrosulphuret of ammonia.

> *a.* NO PRECIPITATE IS FORMED. Pass over to § 122, for neither iron, manganese, cobalt, zinc, nickel, oxide of chromium, nor alumina, are present; nor are the phosphates of the alkaline earths, nor oxalate of lime, barytes, and strontia.
>
> *b.* A PRECIPITATE IS FORMED. The whole fluid is treated in the same manner as the sample.

1. THE PRECIPITATE IS WHITE. Absence of iron, cobalt, nickel. The analyst has to test for all the other metals and compounds enumerated at *a*, since faint tints of sulphuret of manganese and oxide of chromium are obscured entirely in a large bulk of white precipitate. The fluid is filtered off from the precipitate—(the filtrate being kept for subsequent examination, according to the directions of § 122)—and the latter is then washed and subsequently dissolved in hydrochloric acid.* The

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* If the precipitate is inconsiderable, this may be effected best by forcing it to the lower part of the filter, by means of a syringe bottle, allowing the water to run off, and adding hydrochloric acid drop by drop.

solution is boiled, until the odor of sulphuretted hydrogen has *totally* disappeared; the fluid is then filtered, and an excess of solution of potass added drop by drop.

a. THE PRECIPITATE WHICH FORMS AT FIRST UPON THE ADDITION OF THE POTASS, REDISSOLVES COMPLETELY IN AN EXCESS OF THE PRECIPITANT. Absence of the phosphates and oxalates of the alkaline earths, and of manganese. Presence of ALUMINA or OXIDE OF ZINC, (and perhaps also of oxide of chromium which, if present to any perceptible amount, will impart a green appearance to the potass solution.) The solution is divided into two parts, and one portion is acidified with hydrochloric acid, ammonia in excess added, and the fluid heated for a short time.

α. *No permanent precipitate is formed.* Absence of alumina and of oxide of chromium. Solution of sulphuretted hydrogen is added to the other portion of the potass solution. The formation of a white precipitate indicates ZINC.

β. *A permanent precipitate is formed.* The precipitate is filtered off, and should a green coloration of the potass solution, or a green, yellow, or red tint of the original solution lead the analyst to suspect the presence of OXIDE OF CHROMIUM, a small portion of it is tested for this substance, with phosphate of soda and ammonia, (§ 88. *b.* 6.)* Solution of sulphuretted hydrogen is added to the filtrate. The formation of a white precipitate indicates ZINC. The process of testing for alumina proceeds now as follows:

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* For even though chromic acid be present, a precipitate of oxide of chromium will be produced by hydrosulphuret of ammonia, the sulphuretted hydrogen reducing the acid to the oxide. In such cases, the yellow or red color of the solution changes to green upon the addition of the sulphuretted hydrogen, and this change of color is attended with separation of sulphur.

aa. No oxide of chromium has been detected. This is in itself sufficient to prove the presence of ALUMINA. The blow-pipe examination of the precipitate produced by ammonia will lead to a positive conviction on this point. (Vide § 88. *a.* 5.)

bb. Oxide of chromium has been detected. In this case, the second portion of the potass solution is boiled, until the oxide of chromium has completely precipitated; the fluid is then slightly diluted, and filtered off from the precipitated oxide of chromium: the filtrate is acidified with hydrochloric acid, and ammonia in excess added. The formation of a precipitate indicates ALUMINA. The blow-pipe is resorted to as a conclusive test. Should ebullition fail to effect the separation of the oxide of chromium from the potass solution, as may happen under certain circumstances, the precipitate produced by ammonia is to be fused with nitrate of potass and some carbonate of soda, to remove the chromium. (Vide § 88. *b.* 5.) "The alumina may have been present as a PHOSPHATE, and may have been precipitated as such. For the manner of deciding this, I refer to § 113. 1."

b. THE EXCESS OF THE POTASS FAILS TO RE-DISSOLVE THE WHOLE OF THE PRECIPITATE. The solution is filtered off, and the filtrate subsequently treated, according to the directions of § 121. 1. *a.* The residual precipitate may consist of MANGANESE, and "of the PHOSPHATES and OXALATES OF THE ALKALINE EARTHS." If the precipitate acquires a brown color when exposed to the air, this indicates the presence of MANGANESE. The test with carbonate of soda before the blow-pipe is resorted to as a conclusive proof. (§ 89. *b.* 6.) Should manganese be present, the precipitate is to be dissolved in hydrochloric acid; some tartaric acid is added to the solution, and subsequently ammonia in excess. If no precipitation ensues, this proves the absence of the phosphates and oxalates of the alkaline earths; the formation of a precipitate indicates the presence of these compounds. This precipitate (or, in case no manganese was present, the residue which potass has failed to dissolve) is washed and subjected to the following preliminary examination, in order to ascertain whether it consists exclusively of phosphates of the alkaline earths, or of oxalates of the alkaline earths alone, or finally, whether it is a mixture of both. The precipitate is dried, ignited in a small dish, allowed to cool, some water poured over it, and hydrochloric acid added in excess.

α. *It dissolves without effervescence:* absence of oxalates. Presence of a PHOSPHATED ALKALINE EARTH. The solution is treated according to the directions of § 113. 2. *a.*, to demonstrate the presence of the phosphoric acid and discover the bases combined with it.

β. *It dissolves with effervescence:* presence of an OXALATED ALKALINE EARTH. The solution is boiled to expel the carbonic acid, and ammonia is subsequently added in excess.

aa. No precipitate is formed. Absence of phosphates: exclusive presence of an oxalated alkaline earth. The solution is treated according to the directions of § 122; to discover with which of the alkaline earths the oxalic acid was originally combined in the analysed compound.

bb. A precipitate is formed: joint presence of a phosphate and oxalate. The fluid is filtered off from the precipitate, and the filtrate is subsequently tested as in *aa*, for the bases with which the oxalic acid was originally combined. The precipitate is washed, and subsequently treated according to the instructions of § 113. 2. *a.*, to demonstrate the presence of the phosphoric acid and discover the bases combined with it.

2. THE PRECIPITATE PRODUCED BY HYDROSULPHURET OF AMMONIA IS NOT WHITE; this indicates chromium, manganese,

iron, cobalt, or nickel. If the precipitate is black or inclining to black, this is a positive proof of the presence of one of the three latter metals. However this may be, the analyst has at all events to look for the whole of the metals and compounds enumerated at § 121. *a.* The fluid is filtered off from the precipitate, and the filtrate is kept for further examination according to the instructions of § 122. The precipitate is thoroughly washed with water containing some hydrosulphuret of ammonia in admixture, and subsequently treated on the filter with dilute hydrochloric acid (one part of hydrochloric acid to five parts of water).

If the dilute hydrochloric acid fails to dissolve the whole of the precipitate and leaves a black residue, this indicates the presence of cobalt or nickel. If, on the other hand, the precipitate dissolves completely in the dilute acid, this may be considered pretty conclusive of the absence of these two metals. Should the former be the case, a small sample of the undissolved residue is to be tested for cobalt with borax, before the blow-pipe, (§ 89. *d.* 8.) ;—a hole is then pushed through the bottom of the filter, and the residue is rinsed into the solution, by means of a syringe bottle.

No matter whether the precipitate has completely dissolved in the hydrochloric acid or not, some nitric acid is now added to the fluid, and the mixture is then heated to boiling. This serves to effect the solution of the sulphurets of cobalt and nickel on the one hand, and the conversion of the protoxide* of iron into peroxide on the other.

In cases where water failed to dissolve the original substance, or at least the whole of it, and in fact in all cases whenever the solution is acid, it is necessary, in the first place, to ascertain whether phosphates or oxalates of the alkaline earths are present or not.

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* Although the iron may have been present in the original solution, in the form of peroxide, yet the sulphuret of iron which precipitates upon the addition of sulphuretted hydrogen or hydrosulphuret of ammonia, corresponds invariably to the protoxide, since these reagents reduce the peroxide of iron. (§ 89. *f.* 3. and 4.)

For this purpose a small sample of the acid solution is nearly (but not altogether) neutralized with ammonia, and is then mixed with one drop of perchloride of iron, one drop of chloride of calcium, and an excess of acetate of potass. The non-formation of a precipitate demonstrates the absence of phosphates and oxalates of the alkaline earths; the formation of a precipitate indicates the presence of these substances, and the analyst has to shape his course accordingly.

Before proceding further, the analyst should recollect whether the original solution was colorless or colored, since, if the former was the case, the absence of chromium may be considered sufficiently proved, whilst, if the original solution was colored (green, yellow, red, &c.) the presence of chromium must be had regard to in the subsequent analytical process.

a. PHOSPHATES AND OXALATES OF THE ALKALINE EARTHS ARE NOT PRESENT. The solution is mixed with caustic potass in excess, and the mixture is boiled for some time, subsequently diluted with water, and filtered. The *filtrate* is divided into two portions, and sulphuretted hydrogen water added to the one, whilst the other is acidified with hydrochloric acid, and subsequently mixed with ammonia. If the sulphuretted hydrogen produce a precipitate in the first portion, ZINC is present, whilst the formation of a white flocculent precipitate in the other portion indicates the presence of ALUMINA. "Whether this substance is combined with phosphoric acid or not, is subsequently ascertained in the manner described at § 113. 1."

The *precipitate* produced by the potass is washed, and subsequently treated as follows:*

α. *The original solution was colorless, and there is*

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* Should the amount of iron present be very considerable, which might tend to obscure the distinctness of the reactions, the course described at § 121. 2. *b.* β. may be substituted for that described here sub. *a.* α. and β., although the latter is the more simple of the two

accordingly no reason to suspect the presence of chromium.

aa. A portion of the precipitate is tested for MANGANESE, with carbonate of soda, in the outer blow-pipe flame. (§ 89. *b.* 6.)

bb. Should cobalt not yet have been detected (see above, § 121. 2. at the commencement), a second sample of the precipitate is to be tested for COBALT, with borax in the inner blow-pipe flame. (§ 89. *d.* 8.)

cc. The rest of the precipitate is dissolved in hydrochloric acid, and a portion of the solution is subsequently tested for IRON, with ferrocyanide of potassium, acetate of potass having been added previously. To decide whether the detected iron was originally present in the form of peroxide or of protoxide, the original solution in water or in hydrochloric acid (but not in nitric acid) is to be tested with ferro and ferricyanide of potassium (§ 89. *e.* 7. and § 89. *f.* 6.)

dd. The rest of the hydrochloric solution of *cc.* is mixed with a few more drops of hydrochloric acid (if it does not contain already a large proportion of free acid). Cyanide of potassium is then added in excess, the mixture is boiled for some time, filtered, if necessary, and mixed with dilute sulphuric acid. If a light greenish precipitate forms, either immediately or after the lapse of some time, this is a proof of the presence of NICKEL (§ 89. recapitulation and remarks.)

β. The original solution was colored, and there is accordingly reason to suspect the presence of chromium.

The precipitate is triturated with one part of carbonate of soda and three parts of nitrate of potass, and the mixture is subsequently fused in a porcelain crucible; the fused mass is then poured upon a broken piece of porcelain—(to preserve the crucible)—and, when cold, reintroduced into the same crucible, and boiled with water, the solution being subsequently filtered off from the undissolved residue.

The *residue* is washed with water, and tested for MANGANESE, COBALT, IRON, and NICKEL, as directed at § 121. 2. *a*. α. The filtrate, which will appear yellow if chromium be really present, is acidified with acetic acid, and acetate of lead added. The formation of a precipitate of chromate of lead is a positive proof of the presence of CHROMIUM.

b. PHOSPHATES OR OXALATES OF THE ALKALINE EARTHS ARE PRESENT.

α. A small portion of the solution is poured into a test-cylinder, and some finely-levigated peroxide of manganese* added, and subsequently a few drops of concentrated sulphuric acid. Ensuing effervescence of carbonic acid indicates the presence of OXALIC ACID. The best way of setting all doubt at rest on this point is, to heat the mixture gently, whilst the cylinder is kept loosely stopped with the thumb. When the evolution of gas has proceeded for some time, the carbonic acid gas accumulated in the cylinder is poured into another cylinder containing some lime-water; this is effected by gently inclining the test-tube, so that the gas alone flows out; the lime-water and carbonic acid in the other tube are then mixed by shaking the tube. The formation of a precipitate (carbonate of lime) is a positive proof of the presence of an OXALATE.

αα *No oxalic acid has been found.* Presence of PHOSPHORIC ACID. A second portion of the hydrochloric solution is mixed with ammonia until the greater part of the free acid is neutralized; a drop of perchloride of iron is then added, and subsequently acetate of potass in excess. The formation of a precipitate confirms the presence of phosphoric acid. Some more perchloride of iron is then added until the fluid appears red; the fluid is then boiled for some time, and subsequently filtered. The filtrate is supersaturated with ammonia, hydrosulphuret of ammonia added, the mixture filtered, and the filtrate finally examined according to the instructions of § 122 and 123, to ascertain which of the alkaline earths were originally combined with the phosphoric acid in the analysed substance.

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* The peroxide of manganese must be perfectly free from admixture of carbonates of the alkaline earths, and is consequently, if necessary, first to be freed from such admixture, by washing with dilute nitric acid.

ββ. *Oxalic acid has been found.* A portion of the hydrochloric solution is boiled for some time with finely levigated peroxide of manganese; this effects the decomposition of the oxalic acid. The fluid is then filtered, and the filtrate tested as in αα. Phosphoric acid and the alkaline earths combined with this and the oxalic acid.

β. The rest of the hydrochloric solution is mixed with potass in excess, the mixture boiled for some time, and subsequently diluted with water; the fluid is then filtered off from the precipitate formed, and the filtrate tested for ZINC and ALUMINA, in the manner described at § 121. 2. *a.*

The precipitate is dissolved in hydrochloric acid—(either directly, or after previous fusion with carbonate of soda and nitrate of potass to detect and separate the CHROMIUM; compare § 121. 2. *a.* α. and β.)—and the solution is then *nearly* evaporated to dryness; the residue is dissolved in water, and an excess of precipitated carbonate of lime (§ 35.) added to the solution; the mixture is shaken for some time, without applying heat, and the fluid is then filtered off from the precipitate, which contains the phosphates and oxalates of the alkaline earths and IRON.

The latter metal is now tested for by dissolving the *precipitate* in hydrochloric acid, diluting the solution considerably, and adding ferrocyanide of potassium. Whether the iron was originally present in the analysed substance, in the form of peroxide, or in that of protoxide, is finally ascertained in the same manner as described at § 121. 2. *a*. α. *cc*.

The *filtrate* is mixed with hydrosulphuret of ammonia.

αα. *No precipitate is formed.* Absence of nickel, cobalt, and manganese.

ββ. *A flesh-colored precipitate is formed.* Absence of nickel and cobalt; presence of MANGANESE. The blow-pipe is resorted to as a conclusive test. (§ 89. *b*. 6.)

γγ. *A black precipitate is formed.* The precipitate is washed, and a small portion of it is subsequently tested for MANGANESE, with carbonate of soda in the outer blow-pipe flame; another portion is tested for COBALT,* with borax, in the inner blow-pipe flame, and the rest is dissolved in aqua regia, and the solution tested for NICKEL, by the method described at § 121. 2. *a*. α. *dd*.

§ 122.

A PORTION OF THE FLUID IN WHICH HYDROSULPHURET OF AMMONIA HAS FAILED TO PRODUCE A PRECIPITATE, OR OF THE FLUID FILTERED OFF FROM THE PRECIPITATED SULPHURETS, IS MIXED WITH PHOSPHATE OF SODA, AND AMMONIA ADDED (SHOULD THE FLUID NOT ALREADY CONTAIN FREE AMMONIA). THE MIXTURE IS VIGOROUSLY SHAKEN.

a. *No precipitate is formed:* absence of the alkaline earths. Another sample of the fluid is evaporated to dryness, and the residue ignited; should it volatilize completely, neither potass nor soda are present: pass over to § 125. Should a residue remain, the rest of the fluid is to be evaporated to dryness, and the residue subsequently ignited, and treated according to the directions of § 124.

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* In cases where the blow-pipe test has demonstrated the presence of manganese, it is advisable, ere testing for cobalt, to remove the sulphuret of manganese by washing with acetic acid, since the presence of manganese tends to impair the distinctness of the cobalt reaction.

b. A precipitate is formed.

The remainder of the fluid is mixed with sal ammoniac, (should this salt not be present already,) and a mixture of carbonate of ammonia with some caustic ammonia added; the whole mixture is then gently heated for some time (but not to ebullition).

1. *No precipitate is formed.* Pass over to § 123, for neither lime, barytes, nor strontia are present.

2. *A precipitate is formed.* Presence of LIME, BARYTES, or STRONTIA. The fluid is filtered off from the precipitate, and the filtrate kept for further examination, according to the directions of § 123. The precipitate is dissolved in the least possible amount of highly dilute hydrochloric acid, and the solution treated as follows:

a. Solution of gypsum is added to a portion of it.

α. *No precipitate is formed,* NOT EVEN AFTER THE LAPSE OF A CONSIDERABLE TIME. Pass over to § 122. 2. *b.*, for neither barytes nor strontia are present.

β. *A precipitate is formed.*

aa. It is formed immediately upon the addition of the solution of gypsum: this indicates BARYTES. Besides this substance, strontia and lime may be present.

A portion of the hydrochloric solution of the precipitate, produced by carbonate of ammonia, is evaporated to dryness, and the residue digested with absolute, or, at all events, very strong alcohol; the solution is filtered, and a few drops of the filtrate are evaporated upon a platinum plate.

αα. No residue remains: pass over to § 123; for neither strontia nor lime are present.

ββ. A residue remains. The alcoholic solution is divided into two portions, of which the one is heated in a small crucible and kindled: a carmine-red tint of the flame indicates STRONTIA. Should the flame not appear red, or should any doubt exist on this point, the second portion of the alcoholic solution is to be evaporated to dryness, the residue subsequently dissolved in a small quantity of water, and the solution finally tested with solution of gypsum. The formation of a precipitate, after the lapse of some time, indicates STRONTIA.

The presence of barytes may be positively demonstrated by adding hydrofluosilicic acid to the hydrochloric solution, and applying heat. The formation of a crystalline precipitate after the lapse of some time, proves the presence of BARYTES. (§ 87. *a.* 6.)

bb. The precipitate forms only after the lapse of some time: absence of barytes: presence of STRONTIA.

b. A fresh portion of the hydrochloric solution of the precipitate produced by carbonate of ammonia, is made alkaline by addition of ammonia, and subsequently tested for lime, with oxalic acid. Should the preceding examination (§ 122. 2. *a. β.*) have revealed the presence of barytes or strontia, these earths must first be removed from the hydrochloric solution before the latter can be tested for lime; for this purpose sulphate of potass or dilute sulphuric acid are added to the hydrochloric solution, and the fluid is then filtered off from the precipitate formed; the filtrate is made alkaline with ammonia, and oxalic acid is then finally added. The formation of a precipitate demonstrates the *presence of lime.*

§ 123.

TAKE TWO SMALL PORTIONS OF THE FLUID IN WHICH CARBONATE OF AMMONIA HAS FAILED TO PRODUCE A PRECIPITATE, OR OF THAT WHICH HAS BEEN FILTERED OFF FROM THE PRECIPI-

TATE FORMED, (§ 121. 1.) AND ADD SOME SULPHATE OF POTASS OR DILUTE SULPHURIC ACID TO THE ONE, AND OXALATE OF AMMONIA TO THE OTHER.

1. BOTH THESE REAGENTS FAIL TO PRODUCE ANY FURTHER PRECIPITATE. This is a positive proof that the barytes, strontia and lime, have been completely precipitated by the carbonate of ammonia. Phosphate of soda is added to a third portion of the fluid, (§ 122. 1.) and the mixture stirred with a glass rod. The formation of a crystalline precipitate, (compare § 87. *d.* 7.) demonstrates the presence of MAGNESIA. No matter whether magnesia has been detected or not, the rest of the fluid (§ 122. 1.) is evaporated to dryness, and the residue heated till all the ammoniacal salts are completely expelled. Should no residue remain, pass over to § 125; if a residue remains, pass over to § 124.

2. BOTH OR ONE OF THE REAGENTS PRODUCE STILL A PRECIPITATE. In that case the carbonate of ammonia has not yet completely removed the whole of the barytes, strontia, and lime. This reagent, mixed with caustic ammonia, is therefore once more added to the rest of the fluid, and the mixture again heated for some time. The precipitate which forms upon this is filtered off, and the filtrate subsequently treated as at 1.

§ 124.

We come now to the examination for fixed alkalies and for ammonia.

The compounds of the former are, with very few exceptions, soluble in water. Substances insoluble in water need therefore usually not be tested for the fixed alkalies.

In the case of substances insoluble in water, but soluble in hydrochloric acid, or in nitric acid, a portion of the fluid in the sample of which phosphate of soda failed to produce a precipitate, (§ 122. *a.*)—or of that in which carbonate of ammonia has produced none, (§ 122. *b.* 1.)—or of that which has been filtered off from the precipitate formed (§ 122. *b.* 2.) should be kept for examination for phosphoric acid and oxalic acid. (See § 128. 8.)

The presence of magnesia renders certain modifications necessary in the method of examining for potass and soda; we have therefore to distinguish two cases, viz.

1. MAGNESIA IS NOT PRESENT. The ignited residue (§ 122. *a.* or § 123. 1.) is dissolved in a small quantity of water, alcohol added to the solution, and the alcoholic mixture heated to boiling, and kindled.

a. THE FLAME IS VIOLET. Absence of soda; probable presence of POTASS.

b. THE FLAME IS YELLOW; presence of SODA. The solution is evaporated to dryness, and the blow-pipe and test with antimoniate of potass are resorted to as conclusive proofs of the presence of soda. (Vide § 86. *b.*) To demonstrate the presence of potass, the residue is dissolved in water, or, better still, in alcohol, if practicable, and one half of the solution mixed with tartaric acid, and the other half with bichloride of platinum. Should potass be present, the tartaric acid, will after the lapse of some time, produce a colorless, granular, crystalline precipitate, and the bichloride of platinum will produce a yellow precipitate. (Vide § 86. *a.*)

2. MAGNESIA IS PRESENT. The ignited residue of § 123. 1. is dissolved in water, and water of barytes, or solution of sulphuret of barium (containing an admixture of caustic barytes) added, as long as a precipitate continues to form. The fluid is then boiled with the precipitate, subsequently filtered off from the latter, and an excess of a mixture of carbonate of ammonia with some caustic ammonia added to the filtrate. A gentle heat is then applied, and continued for some time; the solution is afterwards filtered, the filtrate evaporated to dryness, and the residue ignited, to remove the ammoniacal salts. The ignited residue is finally treated as at 1.

§ 125.

We come now, finally, to the examination for ammonia. A portion of the substance, or fluid, under examination, is treated with concentrated solution of potass, and heat applied. The ammoniacal odor of the evolved gas, and its property of restoring the blue color of reddened litmus paper, and forming white fumes with hydrochloric acid, demonstrate the presence of ammonia. Potass ley often emits some ammoniacal fumes upon ebullition, and may thus lead to mistakes. It may be advisable, therefore, in some cases, to substitute trituration with an excess of hydrated lime and some water, for ebullition, with potass ley.

Compounds in which all the more frequently occurring acids and bases, metals and metalloids, are supposed to be present.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACIDS AND METALLOIDS.

I. *In the absence of Organic Acids.*

§ 126.

1. For the detection of ARSENIOUS and ARSENIC ACID, CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID, compare § 111. 1. and 2.

2. A portion of the solution is mixed with nitrate of barytes, and neutralized with ammonia, should this be required.

a. NO PRECIPITATE IS FORMED. Absence of sulphuric acid, phosphoric acid, boracic acid, chromic acid, silicic acid, oxalic acid, arsenious and arsenic acid.* Pass over to 3.

b. A PRECIPITATE IS FORMED. The fluid is diluted, and hydrochloric acid added; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present.

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* Should an ammoniacal salt be present in the fluid under examination, the non-formation of a precipitate cannot be considered a conclusive proof of the absence of oxalic acid, arsenious and arsenic acid, and more particularly not of that of boracic acid, since the barytes salts of these acids are not insoluble in water, in presence of ammoniacal salts.

3. Nitrate of silver is added to a portion of the solution, this is previously to be EXACTLY neutralized, if acid, by means of ammonia, and if alkaline, by means of nitric acid.*

a. NO PRECIPITATE IS FORMED. Pass over to 4; neither chlorine, iodine, cyanogen, phosphoric acid, silicic acid, oxalic acid, nor chromic acid are present; nor boracic acid, if the solution was not too dilute.

b. A PRECIPITATE IS FORMED. The color of the precipitate is inspected, and the latter is treated with nitric acid.

α. *The precipitate redissolves completely.* Pass over to 4; for neither chlorine, nor iodine, nor cyanogen are present.

β. *A residue remains:* CHLORINE, IODINE, and CYANOGEN. The residue is washed, and subsequently digested with ammonia.

aa. A yellowish residue remains. Iodine. The reaction with starch (vide § 101. *c.*) is resorted to as a conclusive proof of the presence of this element. The solution is filtered off from the undissolved residue, and nitric acid in excess added to the filtrate; if a precipitate is formed, this indicates chlorine or cyanogen, and is to be further examined, as directed in *bb.*

bb. No residue remains; CHLORINE or CYANOGEN; absence of iodine. The ammonical solution is again precipitated with nitric acid. Before proceeding further in this examination, the analyst should ascertain whether cyanogen is present or not. For this purpose a portion of the original solution is mixed with solution of ferroso-ferric oxide of iron, and hydrochloric acid added. The formation of a blue precipitate indicates the presence of CYANOGEN.* But if no precipitate forms, and the fluid does not acquire a blue tint, shows that the precipitate redissolved by the ammonia consists of chloride of silver alone, and there is no necessity for further examination. But if this preliminary examination has revealed the presence of cyanogen, the precipitate produced by nitric acid in the ammoniacal solution is to be further examined, to distinguish between the chloride of silver and cyanide of silver. The precipitate is accordingly washed, taken from the filter while still moist, dried in a porcelain crucible, and ignited; when the chloride of silver will simply fuse, whilst the cyanide will undergo reduction, attended with formation of some paracyanide of silver. The presence of chlorine may now be readily demonstrated, by placing a fragment of zinc upon the residual mass, pouring water over it which contains some sulphuric acid in admixture, waiting until the evolution of hydrogen ceases, filtering, diluting the filtrate with water, and adding solution of nitrate of silver.

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* This operation offers no difficulty and requires but little time for its performance, if the analyst has taken care to dilute the nitric acid or ammonia considerably.

4. The aqueous solution is tested for NITRIC ACID, by mixing with solution of indigo until the fluid acquires a light blue tint, adding some sulphuric acid, and applying heat; and also by mixing the solution with the third of its amount of concentrated sulphuric acid, and throwing a crystal of protosulphate of iron into the mixture. The presence of nitric acid is demonstrated, in the first case, by the decoloration of the blue solution, and, in the second case, by the formation of a brown zone around the crystal. (§ 102. *a.*)

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* Should the cyanogen be present as free hydrocyanic acid, which may be readily recognized by its characteristic odor, this acid is to be saturated with potash before adding the solution of ferroso-ferric oxide. That nitrate of silver fails to detect the cyanogen in some compounds, (in cyanide of mercury, for instance,) has been mentioned already at § 101. *d.*

I have now still to speak of the examinations for phosphoric acid, boracic acid, silicic acid, oxalic acid, and chromic acid. Testing for these acids is necessary only in cases where both chloride of barium and nitrate of silver have produced precipitates in neutral solutions. Compare note to § 126. 2. *a*.

5. If the precipitate produced by nitrate of silver be of a yellowish color, the analyst has to look more particularly for the presence of phosphoric acid. To detect this acid, ammonia in excess is added to a portion of the fluid: should this produce a precipitate, the fluid is to be filtered off, and chloride of ammonium added to the filtrate, and subsequently sulphate of magnesia. The formation of a crystalline precipitate demonstrates the presence of PHOSPHORIC ACID. The reaction with perchloride of iron and acetate of potass, which I have described at § 99. *a*. 8, may likewise be had recourse to.

6. A small portion of the substance under examination is drenched with alcohol, sulphuric acid added, and the mixture heated to boiling in a small crucible; the alcohol is then finally kindled. If the flame presents a green tint, BORACIC ACID is present. Should copper be present, this must be removed first either by means of sulphuretted hydrogen, or by boiling the fluid with an excess of potass.*

7. If the fluid become red, or yellow changing to red, upon the addition of hydrochloric acid, and if the precipitate produced by nitrate of silver in the neutral solution has a purple red color, the presence of CHROMIC ACID is confirmed.

8. For SILICIC ACID test as § 100. *b*. 2. directs.

9. To effect the detection of OXALIC ACID, solution of gypsum is added to a portion of the fluid under examination, which, should it manifest acid reaction, is to be neutralized with ammonia. The formation of a white precipitate, which addition of acetic acid fails to redissolve, demonstrates the presence of oxalic acid.

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* Should the substance which it is intended to treat for boracic acid be a fluid, this must first be evaporated to dryness, and the residue subsequently operated upon with alcohol and sulphuric acid, in the manner described.

CHLORATES, BROMIDES, and FLUORIDES, are of less frequent occurrence. The presence of chlorates is indicated already by the violent deflagration which ensues upon fusing the salt under examination, in conjunction with charcoal. (Vide § 107. A. I. 2. *c.*) To demonstrate the presence of chloric acid, a sample of the solid salt is heated in a glass tube sealed at one end, and a smouldering wood splinter approached to the open end; when the actual presence of CHLORIC ACID will be confirmed by the kindling of the splinter. Nitrate of silver will, in that case, produce a copious precipitate of choride of silver, in the aqueous solution of the residue. The reaction with concentrated sulphuric acid, (§ 102. *b.* 8.) or fusion with cyanide of potassium, (§ 102. *b.* 4) may likewise be resorted to. The detection of BROMIDES is simple, if iodides are not present at the same time. I refer to § 101 for the way of effecting the positive detection of bromine in either case. With regard to the detection of FLUORIDES, the methods described § 99, *d.* 4 and 6, are the most efficient under all circumstances.

Compounds in which all the more frequently occurring acids and bases, metals and metalloids, are supposed to be present.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACIDS AND METALLOIDS.

II. *In Presence of Organic Acids.*

§ 127.

I. CHROMIC ACID, ARSENIOUS and ARSENIC ACID, have already been detected in the course of testing for the bases; concerning the distinction of arsenious from arsenic acid, compare § 95. additions and remarks.

2. Hydrochloric acid is added to a portion of the solution. The formation of a precipitate which, when heated subsequently on a platinum plate, volatilizes partly or totally, emitting the characteristic odor of BENZOIC ACID, indicates the presence of this acid.

Effervescence, upon the addition of the hydrochloric acid, may be caused by the presence of CARBONIC ACID, or by that of SULPHURETTED HYDROGEN. (Vide § 111. 2.)

3. Ammonia is added to a portion of the solution, until the latter acquires a feebly alkaline reaction; the solution is then filtered, if necessary, chloride of barium added, and the mixture heated to boiling.

Should hydrochloric acid have produced a precipitate in the original solution, the filtrate of this is to be used for this experiment.

a. NO PRECIPITATE IS FORMED. Absence of sulphuric acid, phosphoric acid, chromic acid, silicic acid, boracic acid, arsenic acid, arsenious acid, oxalic acid, tartaric acid, citric acid; these acids may, therefore, be disregarded in the subsequent course of examination. The remarks made in the note to § 126. 2. *a.* apply equally to the last six of these acids.

b. A PRECIPITATE IS FORMED. Dilute hydrochloric acid is added.

α. *The precipitate redissolves:* Absence of sulphuric acid.

β. *A residue remains:* SULPHURIC ACID.

4. Nitrate of silver is added to a portion of the solution, which must first be EXACTLY neutralized with nitric acid, if alkaline, and with ammonia, if acid. (Compare note on page 273.)

a. NO PRECIPITATE IS FORMED: absence of phosphoric acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, citric acid; these may therefore be disregarded in the further course of examination.

b. A PRECIPITATE IS FORMED.

α. *It is white or yellow.* A portion of the fluid, together with the precipitate suspended therein, is boiled. Speedy and complete reduction indicates FORMIC ACID. The reaction with protonitrate of mercury may be had recourse to as a conclusive test. (§ 105. *b.*) I have to refer, however, in this respect, to the remark which will be found at the end of this number, (4.) The rest of the precipitate is treated with nitric acid. If it dissolves, neither CHLORINE, nor IODINE, nor CYANOGEN, are present; but if the nitric acid fails to effect its complete solution, the undissolved residue is to be tested for these salt radicals according to the directions of § 126. 3. *b*. *β*.

β. The precipitate produced by nitrate of silver is purple red: CHROMIC ACID. Should arsenic acid be present, the reaction with acetate of lead must be had recourse to as a conclusive test for chromic acid; this reagent is to be added to a fresh sample of the solution: the formation of a yellow precipitate proves the presence of chromic acid. CHLORINE, IODINE, and CYANOGEN, may likewise be present in the silver precipitate: test for these salt radicals as § 126. 3. *b*. directs.

Should chromic acid be present by the side of formic acid, ensuing reduction of oxide of silver and of protoxide of mercury is not absolutely conclusive of the presence of the latter acid. In this case, the positive proof of the presence of formic acid can be obtained only by the following method: The solution of the compound under examination is distilled in conjunction with some sulphuric acid. The distillate is saturated with soda, and subsequently tested with perchloride of iron (which formic acid tinges blood red) and with nitrate of silver. (Vide § 105. *b*.)

5. Should chloride of barium and nitrate of silver have produced precipitates, the analyst has to test for PHOSPHORIC ACID, according to the direction of § 126. 5, and for SILICIC ACID as directed at § 100. *b*. 2.

6. A portion of the solution which, should its reaction be acid, must be saturated first with potass, is evaporated to dryness, and the residue (or a portion of the original dry substance) introduced into a small tube, some alcohol poured over it, and concentrated sulphuric acid added, to the extent of about one-third of the

volume of the alcohol; the mixture is then heated to boiling. Emission of the odour of acetic ether demonstrates the presence of ACETIC ACID. This odor becomes in many instances more distinctly perceptible on agitating the mixture, whilst cooling or when cold. The contents of the tube are poured into a small crucible, heated, and kindled. Green coloration of the flame denotes the presence of BORACIC ACID.

7. A portion of the fluid is made feebly alkaline by addition of ammonia; the fluid is then filtered, if necessary, and chloride of calcium added. The mixture is vigorously shaken, and subsequently allowed to stand at rest for from ten to twenty minutes. If the solution was neutral, the addition of the chloride of calcium is to be preceded by that of some sal-ammoniac.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of oxalic acid and tartaric acid; pass over to 8.

b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER THE LAPSE OF SOME TIME. The solution is filtered off from the precipitate formed, and the filtrate subsequently tested as directed at 8.

The precipitate is washed and digested cold, with an excess of slightly diluted solution of potass, the operation being aided by agitation of the mixture. The solution is subsequently filtered and the filtrate boiled for some time; should this cause the separation of a precipitate, TARTARIC ACID is present.

Solution of gypsum is added to a portion of the original solution which, if acid, is to be neutralized first with ammonia. The formation of a precipitate, which does not disappear upon the addition of acetic acid, but is re-dissolved by hydrochloric acid, demonstrates the presence of OXALIC ACID.

8. The fluid in which chloride of calcium has failed to produce a precipitate, or that which has been filtered off from the precipitate

formed—(in which latter case some more chloride of calcium is to be added)—is mixed with alcohol.

a. NO PRECIPITATE IS FORMED. Absence of citric acid and of malic acid. Pass over to 9.

b. A PRECIPITATE IS FORMED. The solution is filtered off and the filtrate treated as directed at 9. The precipitate is washed with alcohol, and dissolved, on the filter in the least possible amount of dilute hydrochloric acid; the solution is mixed with ammonia to feebly alkaline reaction, heated to boiling, and kept for some time in ebullition.

α. THE FILTRATE REMAINS CLEAR. Absence of citric acid. Presence of MALIC ACID; alcohol is again added to the fluid, and the lime precipitate which forms is subsequently ignited, when the actual presence of malic acid will be demonstrated by the conversion of the precipitate into carbonate of lime, attended with separation of charcoal; the reaction with acetate of lead is finally resorted to as a confirmatory proof. § 103. *e.* 5.

β. A HEAVY, WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. The solution is filtered whilst boiling, and the filtrate tested for malic acid, in the same manner as at *α*.

9. The filtrate of 8. *b.* (or the fluid in which addition of alcohol has failed to produce a precipitate, § 127. 8. *a.*) is heated to expel the alcohol, and subsequently exactly neutralized with hydrochloric acid; perchloride of iron is then added to the neutralized fluid. Should this fail to produce a light brown flocculent precipitate, neither succinic nor benzoic acid are present. The formation of a precipitate of this kind, on the other hand, proves the presence of SUCCINIC ACID, unless the previous examination should have revealed the presence of benzoic acid. Should this have been the case, the solution is to be filtered off, and the precipitate washed and subsequently digested with ammonia in excess; the mixture is then to be filtered, the filtrate slightly evaporated, and finally

tested for SUCCINIC ACID; with chloride of barium and alcohol. (Compare § 104. additions and remarks.)

10. Test for NITRIC ACID according to the directions of § 126. 4.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID. DETECTION OF THE ACIDS AND METALLOIDS.

I. *Absence of Organic Acids.*

§ 128.

In the examination of these compounds the analyst has to look for all the acids occurring at § 126. with the single exception of chloric acid. Cyanogen compounds are not examined after this method: compare § 131.

1. The remarks made at § 114. 2. upon ARSENIOUS and ARSENIC ACID, HYDROSULPHURIC ACID, CARBONIC ACID, and CHROMIC ACID, apply equally here.

2. A portion of the substance is boiled with nitric acid, and the solution filtered, should any residue remain.

a. Effervescence takes place; this may be caused by CARBONIC ACID, or NITRIC OXIDE GAS; the presence of the former may be demonstrated according to the directions of § 100. *a.* 3.; the latter indicates usually the presence of a sulphur compound.

b. Violet fumes escape, which impart a blue tint to starch: IODINE.

3. Nitrate of silver is added to a portion of the nitric acid solution.

a. NO PRECIPITATE IS FORMED: absence of chlorine; pass over to 4.

b. A PRECIPITATE IS FORMED. The solution is filtered off, and the precipitate washed, and subsequently digested with ammonia; if it redissolves totally or partly, CHLORINE is present.

4. A portion of the substance under examination is boiled with hydrochloric acid, and the solution subsequently filtered, if necessary. A portion of the solution or filtrate is mixed with chloride of barium, after previous dilution with water. The formation of a precipitate indicates SULPHURIC ACID.

5. Another portion of the hydrochloric acid solution is tested for NITRIC ACID, with indigo and protosulphate of iron. (Vide § 126. 4.) In many instances, the presence of the nitric acid will have been revealed already at an early stage of the examination, by the deflagration which ensues upon exposing nitrates, on a charcoal support, to the blow-pipe flame.

6. Should the test of § 128. 2. *b.* not yet have revealed the presence of iodine, a portion of the substance under examination is to be heated with concentrated sulphuric acid. If any IODINE compound be present, violet vapors will be evolved, which impart a blue tint to starch. (Compare § 101. *c.* 7.)

7. Test for BORACIC ACID by treating a sample of the substance with sulphuric acid and alcohol. (Vide § 99. *b.* 5.)

8. The fluid of § 124, from which the metals have been removed, and which has been reserved for this stage of the examination, according to the directions of that paragraph, is now tested for PHOSPHORIC ACID and OXALIC ACID, as directed at § 126. 5. and 9. Should these two acids have been combined with barytes, strontia, and lime, (or the phosphoric acid with magnesia,) their presence will have been revealed already in the course of the examination for the bases.

9. Test for SILICIC ACID as directed at § 100. *b.* 3. With regard to the more rarely occurring BROMINE and FLUORINE compounds, I refer to the remarks made at the end of § 126.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

A 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, AND IN NITRIC ACID. DETECTION OF THE ACIDS AND METALLOIDS.

II. *In presence of Organic Acids.*

§ 129.

1. Test for CARBONIC ACID, ARSENIC ACID, ARSENIOUS ACID, SULPHURIC ACID, NITRIC ACID, BORACIC ACID, CHROMIC ACID, SILICIC ACID, CHLORINE, IODINE, and SULPHUR, as directed at § 128; and for ACETIC ACID as directed at § 127. 6. CYANOGEN compounds are not examined after this method: compare § 131.

2. A portion of the compound under examination is dissolved in hydrochloric acid, and the solution filtered off from the undissolved residue which may remain, and which is subsequently to be tested for BENZOIC ACID, as directed at § 127. 2. The filtrate is mixed with an excess of solution of carbonate of potass, and the mixture boiled for some time. The fluid is filtered off from the precipitate formed, and the filtrate saturated with dilute hydrochloric acid, and subsequently tested for PHOSPHORIC ACID and OXALIC ACID, as directed at § 126. 5. and 9.; and for TARTARIC ACID, CITRIC ACID, MALIC ACID, SUCCINIC ACID, and BENZOIC ACID, strictly according to the directions of § 127. 7. 8. and 9.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids are supposed to be present.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE BOTH IN WATER AND IN HYDROCHLORIC ACID. DETECTION OF THE BASES, ACIDS, AND METALLOIDS.

§ 130.

The following substances and compounds belong to this class:

SULPHATE OF BARYTES, SULPHATE OF STRONTIA, SULPHATE OF LIME, CHLORIDE OF SILVER, CHLORIDE OF LEAD, SULPHATE OF LEAD, SULPHURET OF MERCURY, BISULPHURET OF MERCURY, PROTOCHLORIDE OF MERCURY, SEVERAL OF THE FERRO and FERRICYANIDES, SEVERAL SULPHURETS, SILICIC ACID, SULPHUR and CARBON.

Besides these, a few acid arseniates belong to this class; they are, however, of as rare occurrence in the analysis of the more important—(in a pharmaceutical and technical point of view)—mixtures and compounds, as the insoluble modification of the oxide of chromium, the ignited peroxide of tin, and the fluoride of calcium. Of these latter less frequently occurring substances, I purpose to treat separately.

With regard to the insoluble cyanides, I refer to § 131.

A. THE RESIDUE IS WHITE. It may in that case contain of the above enumerated substances: SULPHATE OF BARYTES, SULPHATE OF STRONTIA, SULPHATE OF LIME, SULPHATE OF LEAD, CHLORIDE OF LEAD, CHLORIDE OF SILVER, PROTOCHLORIDE OF MERCURY, SILICIC ACID, SULPHUR.

No attention need be paid to the presence of sulphate of lime, unless this substance has been detected already in the aqueous solution. The lead compounds also may be disregarded, if the previous examination has not already revealed their presence.

1. A sample of the substance under examination is heated on a platinum plate, and the flame made to play upon it. Emission of the odor of sulphurous acid demonstrates the presence of SULPHUR. If no residue remains, this is a sign of the exclusive presence of sulphur. If the heat applied was very intense, protochloride of mercury may likewise have volatilized. The outward appearance of the residue will suffice to show whether this is to be apprehended.

2. Hydrosulphuret of ammonia is added to a very small portion of the substance under examination.

a. It remains white. Absence of metal compounds. Pass over to 3.

It turns black. This is a positive proof of the presence of a metallic salt, which may be either protochloride of mercury, chloride of silver, chloride of lead, or sulphate of lead. Moreover, all the other compounds enumerated under A. may be present. The further process varies according to the presence or absence of lead.

The following preliminary test is applied to ascertain which method ought to be pursued:

A small portion of the substance is mixed with carbonate of soda, and the mixture exposed to the reducing flame of the blow-pipe. The production of a metallic grain, (which is oxidized in the outer flame,) attended with yellow incrustation of the charcoal, indicates lead.

a. THIS PRELIMINARY EXAMINATION INDICATES THE PRESENCE OF LEAD IN THE WHITE RESIDUE.

aa. The greater portion of the residue (which, if moist, must be dried first) is fused with three parts of dry carbonate of soda and three parts of cyanide of potassium, in a small porcelain crucible, over a spirit-lamp. The mass fuses readily; it is maintained in a state of fusion for some time, and subsequently allowed to cool. The refrigerated mass is boiled with water, the fluid is filtered off from the residue, and the latter very carefully washed. The greater portion of the filtrate is supersaturated with hydrochloric acid, and a sample of this acidified solution tested with chloride of barium. The formation of a precipitate indicates the presence of a SULPHATE. (Should a precipitate (silicic acid) be formed, upon supersaturating the filtrate with hydrochloric acid, the fluid is to be diluted, and subsequently filtered of from the precipitate formed, the filtrate being then finally tested for sulphuric acid.) The rest of the acidified portion of the filtrate is evaporated to dryness, and the residue subsequently treated with water. Should a residue remain, this consists of SILICIC

ACID. The formation of a clear glass, upon fusing the residue with carbonate of soda in the blow-pipe flame, is a conclusive proof of the presence of silicic acid. The rest of the filtrate, which has not been mixed with hydrochloric acid, is acidified with nitric acid, and boiled until it ceases to emit the slightest odor of hydrocyanic acid; nitrate of silver is then added; the formation of a precipitate of chloride of silver denotes that the residue, insoluble in water and hydrochloric acid, contains a CHLORIDE, (provided always, the reagents used be free from chlorine, and the residue thoroughly washed.) The residue which remained upon treating the fused mass with water, and which has been thoroughly washed, is now treated with acetic acid; if it dissolves partly in this acid with effervescence, this is a positive proof of the presence of sulphates of the alkaline earths. If no effervescence takes place, this proves the absence of the sulphates of the alkaline earths; the residue is accordingly at once treated with nitric acid, and the further operation conducted as will be stated immediately. If effervescence has taken place, a sample of the acetic acid solution is tested with sulphuretted hydrogen. If a black precipitate (sulphuret of lead) forms, the lead is removed in the same manner from the whole of the acetic acid solution, and the filtrate—(which, if necessary, is to be concentrated first by evaporation)—treated as § 122. directs, beginning at 2. *a*. Should the sample of the acetic acid solution remain unaltered when tested with the sulphuretted hydrogen, the rest of the solution is treated at once according to the directions of § 122. 2. *a*. The residue, which the acetic acid has failed to dissolve, is treated with nitric acid, and a small portion of the solution subsequently tested with sulphuric acid for lead, after having previously removed the excess of the acid by evaporation. The rest of the solution is considerably diluted with water, and subsequently tested for SILVER, with hydrochloric acid. If nitric acid leaves a residue, this consists of undecomposed silicic acid, or of an incompletely decomposed sulphate of one of the alkaline earths.

bb. Half of the remainder of the residue is boiled with carbonate of potass. Should this change the white color of the residue to grey or black, PROTOCHLORIDE OF MERCURY is present. To obtain positive conviction on this point, the other half is to be heated in a small glass tube, in conjunction with dry carbonate of soda. (Vide § 91. *b.* 8.)

β. THE PRELIMINARY EXAMINATION PROVES THAT THE WHITE RESIDUE CONTAINS NO LEAD. The whole of the residue is drenched and digested for some time, with hydrosulphuret of ammonia in excess, the fluid is filtered off from the precipitate formed, and the latter is washed and subsequently boiled with nitric acid.

aa. The precipitate dissolves, with the exception of the separated sulphur. CHLORIDE OF SILVER alone is present. In confirmation, the nitric acid solution is tested for silver, with hydrochloric acid. To demonstrate the presence of the chlorine, the fluid filtered off from the sulphuret of silver formed is supersaturated with nitric acid, boiled in order to expel the sulphuretted hydrogen, and subsequently filtered off from the sulphur which has separated; the filtrate is then finally tested with nitrate of silver.

bb. A residue remains, besides the separated sulphur.

αα. THIS RESIDUE IS BLACK: MERCURY. The fluid is filtered off from the residue, and the filtrate tested for silver, with hydrochloric acid; the residue is heated with aqua regia. Should this effect complete solution, with the exception of the separated sulphur, the investigation may be considered at an end, the absence of the sulphates of the alkaline earths and that of silicic acid being fully proved;—should a white residue remain, this is to be washed, and subsequently treated as directed at § 130. A. 3. The solution in aqua regia is tested with a clean piece of copper, or with protochloride of tin to obtain positive proof of the presence of mercury, (vide § 120. 2.)

To demonstrate the presence of the chlorine, the sulpharmoniated fluid filtered off from the mixed precipitate is treated as directed at *aa.*

ββ. THE RESIDUE IS NOT BLACK: absence of mercury. For the further process, vide 3.

3. This residue (*ββ*) or the original residue of § 130. A. 2. *a.*, is fused in a platinum crucible,* over a spirit-lamp with double draught, in conjunction with four parts of carbonate of potass and soda; the fused mass is soaked in water, boiled, filtered, and the residue which may remain washed until chloride of barium ceases to produce a precipitate in the rinsing water. (This water must not be added to the filtrate.) The residue is treated as directed at 4. The filtrate is supersaturated with hydrochloric acid, and a portion of it tested with chloride of barium; the formation of a precipitate indicates the presence of SULPHATES OF THE ALKALINE EARTHS. The rest of the filtrate is evaporated to dryness and the residue subsequently treated with water; should an undissolved residue remain, this consists of SILICIC ACID.

4. The residue remaining upon boiling the fused mass with water, (vide 3.) denotes the presence of SULPHATES OF THE ALKALINE EARTHS. It is carefully washed and subsequently treated with hydrochloric acid. Should the residue dissolve totally or partly, either solution being attended with effervescence, this is a

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* A porcelain crucible may be substituted for a platinum crucible, in which case, six parts of a mixture of equal parts of dry carbonate of soda and cyanide of potassium must be employed, instead of the carbonate of potass and soda; the method in the text is however the best.

positive proof of the presence of sulphates of the alkaline earths. The hydrochloric acid solution is then tested according to the directions of § 122., beginning at 2. *a.* Should the hydrochloric acid leave a residue undissolved, this consists of silicic acid or of an imperfectly decomposed sulphate of one of the alkaline earths.

B. THE RESIDUE IS NOT WHITE. The presence of some substances (cinnabar, sulphuret of arsenic) may, in that case, be inferred from the mere color of the residue.

1. Test for SULPHUR, according to the directions of § 130. A. 1.

2. The greater portion of the residue is treated with aqua regia and the mixture boiled; the solution is filtered whilst still hot, and, should any residue remain, besides the separated sulphur, this is once more boiled with water, the fluid subsequently filtered, and this second filtrate added to the first. The whole of the filtrate is then evaporated nearly to dryness, the residual mass redissolved in some water, and one portion of the solution tested for LEAD with sulphuric acid, another portion for MERCURY with a clean piece of copper. If a solution in hydrochloric acid has been used in the examination for the bases (§ 109.), the solution in aqua regia must be tested for the metals in the usual way, since various other sulphurets, insoluble or sparingly soluble in hydrochloric acid, might be present.

3. If aqua regia has left an undissolved residue, besides sulphur, which may have separated, this residue is to be thoroughly washed. Should a compound of lead have been present, hot water is to be used for the rinsing, and the process continued until hydrosulphuret of ammonia ceases to blacken the fluid which runs off.

a. THE RESIDUE IS WHITE: a portion of it is tested with hydrosulphuret of ammonia.

α. *It becomes black.* The whole of the residue is digested with hydrosulphuret of ammonia, and the further process conducted in strict conformity with the directions of § 130. A. 2. *b*. *β*.

β. *It remains white.* The residue is treated as directed at § 130. A. 3.

b. THE RESIDUE IS BLACK; this indicates the presence of carbon in some form: charcoal, coal, bone-coal, graphite, &c. The residue is ignited in a small platinum spoon, or in the blow-pipe flame. If it is entirely consumed this is a proof of the exclusive presence of carbon, but if a residue remains, or if the combustion is not complete (graphite), the analyst has to look likewise for CHLORIDE OF SILVER, SULPHATES OF THE ALKALINE EARTHS and SILICIC ACID; the residue in that case is treated as directed at § 130. B. 3. *a*. *α*.

Of the acids and electro negative substances, CHLORINE and SULPHURIC ACID alone can be present besides those already mentioned. To detect chlorine and sulphuric acid, part of the residue insoluble in hydrochloric acid is digested with hydrosulphuret of ammonia, the solution is divided into two parts, and one half boiled with hydrochloric acid in excess, the other half with nitric acid in excess; both solutions are filtered, and the hydrochloric acid fluid is tested with chloride of barium for sulphuric acid, the nitric acid fluid with nitrate of silver for chlorine.

The insoluble PEROXIDE OF TIN and OXIDE OF CHROMIUM may be detected before the blow-pipe. Peroxide of tin, when exposed on charcoal to the reducing flame of the blow-pipe, with carbonate of soda and cyanide of potassium, yields a soft metallic grain, without incrustation of the charcoal. Oxide of chromium, which is moreover distinguished by its green color, is treated with microcosmic salt, as directed at § 88. *b* 6., or fused with carbonate of soda and nitrate of potass (§ 88. *b*. 5.) The arsenic acid of the insoluble ARSENIATES is detected before the blow-pipe and by reduction in a glass tube. (Vide § 95. *d*.) To effect the detection of the bases, these insoluble arseniates must be decomposed first by boiling with concentrated sulphuric acid. FLUORIDE OF CALCIUM is decomposed by concentrated sulphuric acid, in a platinum crucible: the fluorine is detected by its property of etching glass; the lime remains as gypsum. There are still several other compounds which are rendered insoluble in acids by ignition, but it would exceed the limits of this work to treat of them all.

§ 131.

SPECIAL METHOD FOR THE DECOMPOSITION OF CYANIDES, FERROCYANIDES, &c.* WHICH ARE INSOLUBLE IN WATER.

The analysis of compounds of this description by the general method, gives rise frequently to the manifestation of fallacious phenomena which tend to mislead the analyst. Acids fail moreover frequently to effect the complete solution of these compounds. For these reasons it is advisable to analyze them by the following special method: The substance which it is intended to analyze, is thoroughly extracted with water; the residue is boiled with strong potass ley, and subsequently, after the mixture has been in ebullition a few minutes, some solution of carbonate of potass added, and the whole mixture finally boiled once more.

a. COMPLETE SOLUTION ENSUES. Absence of alkaline earths, nickel, cadmium, bismuth, and silver. Sulphuretted hydrogen water is added in excess to the alkaline solution:

α. *No permanent precipitate is formed.* Absence of zinc, lead, copper.† Nitric acid is added to the alkaline fluid to acid reaction, and subsequently, should the mixture not yet smell strongly of sulphuretted hydrogen, an excess of solution of the latter reagent.

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* The student is advised to read the additional remarks to § 131. (vide section II.) before entering upon this course of analysis.

† I have included oxide of copper among the number of oxides which are soluble in potass, because the hydrated oxide of copper remains suspended in concentrated potass ley in a state of extreme division, and does not separate even upon boiling: the blue fluid which is thus produced looks so like a real solution that it can scarcely be distinguished from one.

aa. No precipitate is formed. Absence of mercury, tin, arsenic, antimony, gold, and platinum. The solution can contain only alumina, and those metals which form compound radicals with cyanogen. A sample of the fluid is tested for CYANOGEN, by successive addition of potass, solution of ferrosoferric oxide, and hydrochloric acid. The rest of the fluid is evaporated to dryness and the residue heated to fusion. The fused mass is poured out upon a broken piece of porcelain, and subsequently boiled with water; the solution is then filtered off from the residue, which is subsequently tested for IRON, MANGANESE, COBALT, and ALUMINA. The filtrate is tested for CHROMIC ACID (in which form the analyst will obtain the whole of the chromium present) with acetate of lead, after previous addition of acetate of potass; and for the other acids which may be present, according to the directions of § 126.

bb. A precipitate forms. The fluid is filtered off from the precipitate, which is then examined for mercury, and the metals of the sixth group, according to the directions of § 118. 3. The filtrate is tested for cyanogen, alumina, iron, manganese, cobalt, chromium, and the acids, as directed at *aa.*

β. A precipitate is formed. The fluid is filtered off from the precipitate, which is subsequently dissolved in nitric acid, and the solution treated according to the directions of § 117. III., bearing in mind that ZINC, LEAD, COPPER (and MERCURY) alone can be present. The filtrate is treated according to the directions of § 131. *a. a.*

b. AN UNDISSOLVED RESIDUE REMAINS. Water is added to the alkaline fluid; the mixture is then boiled once more, and subsequently filtered. The residue is dissolved and examined according to the directions of § 109. A. 2. The filtrate is treated as directed at § 131. *a.*

§ 132.

GENERAL RULES FOR THE DETECTION OF INORGANIC SUBSTANCES IN CASES WHERE ORGANIC SUBSTANCES ARE PRESENT, WHICH BY THEIR COLOR, CONSISTENCE, OR OTHER PROPERTIES, IMPEDE THE APPLICATION OF THE REAGENTS, OR OBSCURE THE PHENOMENA PRODUCED.

Cases of this kind, as I have stated already in my introductory remarks to Part II., are so manifold, that it is impossible to lay down a method for every individual case; I will therefore confine myself here to the description of a few methods, such as are most generally applicable, and leave the adaptation of the modifications which individual cases may require, to the judgment of the analyst.

1. THE SUBSTANCE DISSOLVES IN WATER, BUT THE SOLUTION IS DARK COLORED, OR OF A SLIMY CONSISTENCE.

a. A portion of the solution is boiled with hydrochloric acid, and chlorate of potass gradually added until the mixture appears decolored and perfectly fluid; the solution is then heated until it ceases to emit the odor of chlorine; it is now diluted with water, and filtered. The filtrate is examined in the usual way, beginning at § 118.

b. Another portion of the solution is boiled for some time with nitric acid, subsequently filtered, and the filtrate tested for silver, potass, and hydrochloric acid. This method is frequently preferable to all others in cases where the nitric acid succeeds in effecting the ready and complete destruction of the coloring and slimy matters, &c.

c. ALUMINA and OXIDE OF CHROMIUM might escape detection by this method, because ammonia and hydrosulphuret of ammonia fail to precipitate these oxides from fluids containing non-volatile organic substances in admixture. Should the analyst have reason, therefore, to suspect the presence of these oxides, he must deflagrate a third portion of the substance with nitrate of potass and some carbonate of soda, and boil the fused mass subsequently with water, when the chromium will be obtained in the solution, in the form of chromic acid, whilst the alumina will be found in the undissolved residue.

2. Boiling water fails to dissolve the substance, or effects only partial solution.

The solution is filtered, and the filtrate treated either as directed at § 117, or, should it require decoloration, in conformity with the directions of § 132. 1. Should the solution not admit of filtration, the further operation must be conducted as directed § 132. 2. *c*. The residue may be of various nature:

a. It is fatty. The fatty matters are removed by means of ether, and should any residue remain, this is treated as directed at § 109.

b. It is resinous. Alcohol is used instead of ether, or both liquids are applied successively.

c. It is of a different nature, e. g. organic fibre, &c. The residue is dried, and the greater portion of it triturated with from three to four parts of pure nitrate of potass; the mixture is gradually deflagrated in a red-hot crucible. The residue is treated as § 109. A. directs. Another portion of the original residue is boiled with aqua regia, the solution filtered, and the filtrate tested for mercury. The other part of the original residue is tested for ammonia, according to the directions of § 125.

§ 133.

IV. CONFIRMATORY EXPERIMENTS.

When the various bases, acids, and electro-negative bodies, present in the substance under examination have been detected, it is in many cases *advisable*, and in others even absolutely *necessary*, to control the results obtained. Many substances are so distinctly characterized by certain reactions, that their positive detection may be readily effected, even though the compound or mixture under examination, may contain a great many other substances. It is simply necessary for this purpose to call forth their characteristic reactions in some fresh samples of the analyzed body. But there are, on the other hand, a great many substances deficient in characteristic reactions. In the case of substances of this latter description, the analyst should invariably endeavour to ascertain by the strictest examination into the attendant circumstances, whether the reactions and phenomena which lead him to assume the presence of a certain substance may not be owing to extraneous causes. How often does it happen, for instance, that the presence of ammonia in a substance is deemed fully demonstrated, whilst in reality the reactions leading to this assumption, are owing simply to the presence of ammonia in the atmosphere of the laboratory? How often is the presence of alumina unhesitatingly pronounced, simply because the potass ley used becomes turbid upon the addition of solution of sal ammoniac, when the real cause of this turbidity is impurity of the ley, &c.

As I have already in the preceding part of the work, fully discussed the subject of reagents and reactions I have only to observe that the selection of methods best adapted to control the results of any given analysis must be left to the discernment of the analyst.

CHAPTER II.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. ADDITIONAL REMARKS TO THE PRELIMINARY EXAMINATION.

To §§ 106—108.

The inspection of the physical properties of a body may, as I have stated at § 106, in many cases enable the analyst to draw certain general (at least negative) inference as to its nature. Thus, for instance, if the analyst is examining a white substance, he may at once conclude that it is not cinnabar or, if a light substance, that it is not a compound of lead, &c.

Inferences of this kind are quite admissible to a certain extent; but if carried too far they are apt to mislead the analyst, by blinding him to every reaction that may militate against his preconceived notions.

With regard to the examination of substances at a high temperature, I may remark that small glass tubes, from two to three inches in length, and sealed at one end, may, in many cases, be substituted for iron spoons. They afford this advantage over the latter, that volatile bodies, organic substances, &c., are less likely to escape detection, and that a more correct and precise notion can be formed of the nature of the heated substance, than were it exposed in an iron spoon, to the action of heat. However, as every experiment would require a fresh tube, a spoon will be found more convenient and economical in experiments for practice.

With respect to the preliminary examination by means of the blow-pipe, I have to remark that the student must avoid drawing positive conclusions from pyrochemical experiments, until he has acquired some practice in this branch of analytical chemistry. A slight incrustation of the charcoal support which may *seem* to denote the presence of a certain metal, is not always a *conclusive* proof of the presence of that metal, nor would it be safe to assume the absence of a substance simply because the blow-pipe flame has failed to effect reduction, &c., &c. The blow-pipe reactions are, indeed, in most cases unerring, but it is not always easy to produce them, and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination ; the notion that this omission will save time and trouble is very erroneous indeed.

II. ADDITIONAL REMARKS TO THE SOLUTION OF SUBSTANCES, &c.

TO § 109.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from *sparingly* soluble to *insoluble* is very gradual. Sulphate of lime (which is soluble in four hundred and thirty parts of water) might perhaps serve as a limit between these two classes, since this salt may still be positively detected in aqueous solution, by the very susceptible reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon a platinum plate, there remains sometimes a very minute residue, which leaves the analyst in doubt with respect to the nature of the substance ; in this case the fluid is, in the first place, to be tested with litmus papers ; a drop of solution of chloride of barium is then to be added to a portion of it, and some carbonate of potass to another portion. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not examine it any further for bases or acids. If the aqueous fluid contained any of those bases or acids which principally form sparingly soluble compounds, the chloride of barium and carbonate of potass would have revealed their presence. The analyst may therefore feel certain that the detection of the substance of which the residue remaining upon evaporation consists, will be more readily effected in the solution in hydrochloric or nitric acid, or aqua regia, as the case may be.

If water has dissolved any part of the substance under examination, the student will always do well to examine this solution for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound under examination—an advantage which will counterbalance the drawback of meeting sometimes with the same substance in the aqueous and in the acid solution.

The following substances are insoluble in water, but soluble in hydrochloric acid or in nitric acid, (with some exceptions) : the phosphates, arseniates, arsenites, borates, carbonates, and oxalates of the earths and metals ; and also several tartrates, citrates, malates, benzoates, and succinates, the oxides and sulphurets of the heavy metals, alumina, magnesia, many of the metallic iodides and cyanides, &c. Nearly the whole of these compounds are decomposed, if not by dilute, yet by boiling concentrated hydrochloric acid, (for the exceptions vide § 130.) but this decomposition gives rise to the formation of insoluble compounds when oxide of silver is present, and of sparingly soluble compounds in the presence of protoxide of mercury and lead. This is not the case with nitric acid, and the latter effects accordingly complete solution in many cases where hydrochloric acid has left a residue. But nitric acid, on the other hand, leaves, besides those substances which are insoluble in simple acids, oxide of antimony, peroxide of tin, peroxide of lead, &c. undissolved, and fails to effect the complete solution of many other substances. When, therefore, the compound under examination is not completely dissolved by nitric acid, (with the exception of the sulphur, which may separate in the case of sulphur compounds,) the analyst is referred again to the hydrochloric solution, and thus exact limits are in some measure assigned to the third class of substances, viz. those which are insoluble in water and simple acids.

With regard to the solution of pure metals or alloys, I have to remark, that white precipitates form frequently upon boiling with nitric acid, although neither tin nor antimony be present. Inexperienced students often confound such precipitates with the oxides of these two metals, although their external appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water. The analyst should consequently ascertain first, whether these white precipitates will dissolve in water or not, before he concludes them to consist of tin or antimony.

III. Additional remarks to the actual examination.

To § 110—§ 132.

A. General survey and explanation of the analytical course.

a. DETECTION OF THE BASES.

The classification of the bases into groups, and the methods which serve to detect and isolate the individual bases, have been fully explained in Part I., Chapter III. The systematic course of analysis from § 117 to § 125, is based upon this classification of the bases; and as a correct apprehension of this is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests—a key, as it were, to the systematic course, as far as the bases are concerned. With respect to the individual detection of the several bases, I refer the student, moreover, to the additions and remarks to § 86—§ 95. The general reagents which serve to divide the bases into principal groups are—HYDROCHLORIC ACID, SULPHURETTED HYDROGEN, HYDROSULPHURET OF AMMONIA, and CARBONATE OF AMMONIA; this is likewise the order of succession in which they are applied. Hydrosulphuret of ammonia performs a *double* part.

Let us suppose we have in solution the whole of the bases, together with arsenious acid, and phosphate of lime, (which latter may serve as a type for the salts of the alkaline earths, which are soluble in acids, and which ammonia re-precipitates unaltered from such solution.)

Chlorine forms insoluble compounds with silver and mercury alone; chloride of lead is sparingly soluble in water. The insoluble protochloride of mercury corresponds with the protoxide of mercury. If, therefore, we add to our solution:

1. *Hydrochloric acid.*

We remove from it the metallic oxides of the first section of the fifth group, viz., the OXIDE OF SILVER and the PROTOXIDE OF MERCURY. From concentrated solutions, a portion of the LEAD may likewise precipitate as chloride; this is, however, immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Sulphuretted hydrogen precipitates the oxides of the fifth and sixth group completely from solutions containing a free mineral acid, since both the affinity which the metallic radicals of these oxides have for sulphur, and that which hydrogen possesses for oxygen, are sufficiently powerful to overcome the affinity between the metal and the oxygen, and that between the oxide and a strong acid, EVEN THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other bases are precipitated under these circumstances, since the bases of the first, second, and third group form no sulphur compounds insoluble in water; and the affinity which the metallic radicals of the oxides of the fourth group possess for sulphur, conjointly with that manifested by hydrogen for oxygen, are not sufficiently powerful to overcome the affinity of the metal for oxygen and of the oxide for a strong acid, IF THE LATTER IS PRESENT IN EXCESS.

Accordingly, after the removal of the oxide of silver and protoxide of mercury, by means of hydrochloric acid, if we add to our solution, (which still contains free hydrochloric acid.)

2. *Sulphuretted hydrogen.*

We remove from it the rest of the oxides of the fifth, together with those of the sixth group, viz., OXIDE OF LEAD, PEROXIDE OF MERCURY, OXIDE OF COPPER, OXIDE OF BISMUTH, OXIDE OF CADMIUM, PEROXIDE OF GOLD, PEROXIDE OF PLATINUM, PROTOXIDE OF TIN, PEROXIDE OF TIN, OXIDE OF ANTIMONY, ARSENIOUS ACID, and ARSENIC ACID. All the other oxides remain in solution, either unaltered or reduced to a lower degree of oxidation, e. g. peroxide of iron, to protoxide; chromic acid, to oxide of chromium, &c.

The sulphurets corresponding to the oxides of the sixth group possess the faculty of combining with electro-positive metallic sulphurets (the sulphurets of the alkali metals) with which they form sulphur salts soluble in water; whilst the sulphurets corresponding to the oxides of the fifth group do not possess this property. If, therefore, we treat the whole of the sulphurets precipitated by sulphuretted hydrogen from acid solution, with—

3. *Hydrosulphuret of ammonia*, or *sulphuret of potassium*,

the bisulphuret of mercury, and the sulphurets of lead, copper, bismuth, and cadmium, will remain undissolved, whilst the other sulphurets dissolve as double sulphurets of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with SULPHURET OF AMMONIUM or POTASSIUM, and re-precipitate from their solution, upon the addition of an acid, either unaltered, or as regards the proto-sulphuret of tin, in a state of higher sulphuration, (the proto-sulphuret of tin absorbs sulphur from the sulphuret of ammonium.) The rationale of this precipitation is as follows:—The acid decomposes the sulphur salt formed. The sulphur base (sulphuret of ammonium or sulphuret of potassium) transposes with the constituents of the water, to an oxygen base (oxide of ammonium or potass) and sulphuretted hydrogen; the former combines with the acid added, the latter escapes, and the liberated electronegative sulphuret precipitates. (If the acid is an hydracid, the radical combines with the ammonium and the hydrogen with the sulphur.) Sulphur precipitates at the same time, the hydrosulphuret of ammonia containing invariably an excess of sulphur. The analyst must bear in mind that the thus eliminated sulphur makes the color of the precipitated sulphurets appear lighter than they are naturally.

Of the oxides still in solution, the alkalies, the alkaline earths, alumina and oxide of chromium have remained so, because their sulphur compounds are soluble in water, or because their salts are not at all affected by sulphuretted hydrogen; the sulphurets corresponding to the oxides of the fourth group, are insoluble in water, and would have been precipitated accordingly by sulphuretted hydrogen, had not the free acid present prevented their precipitation. If, therefore, this free acid be removed, i. e. if the solution be made alkaline and sulphuretted hydrogen added, or if, what answers both purposes at once,

4. *Hydrosulphuret of ammonia*

be added to the solution, the sulphurets corresponding to the oxides of the fourth group will precipitate, viz.: SULPHURET OF IRON, SULPHURET OF MANGANESE, SULPHURET OF COBALT, SULPHURET OF NICKEL, and SULPHURET OF ZINC. Conjointly with these sulphurets, **ALUMINA**, **OXIDE OF CHROMIUM**, and **PHOSPHATE OF LIME**, are precipitated, because the affinity which the oxide of ammonium possesses for the acid of the salt of alumina or of oxide of chromium, or for the acid which keeps the phosphate of lime in solution, induces the elements of the sulphuret of ammonium, to transpose with those of the water, giving thus rise to the formation of oxide of ammonium and of sulphuretted hydrogen. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated oxides, or with the phosphate of lime,—the oxides and the limesalt precipitate. There remain now in solution only the alkaline earths and the alkalies. The neutral carbonates of the former are insoluble in water, whilst those of the latter are soluble in that menstruum. If, therefore, we add now

5. *Carbonate of ammonia,*

and apply heat, in order to decompose the bicarbonates which may have been formed, the whole of the alkaline earths ought to precipitate. This is, however, the case only as regards BARYTES, STRONTIA, and LIME ; of magnesia we know that, owing to its disposition to form double compounds with ammoniacal salts, it precipitates only in part; and that the presence of additional ammoniacal salts prevents its precipitation altogether. To prevent any uncertainty arising from this, sal ammoniac is added previously to the carbonate of ammonia, and thus the precipitation of the magnesia is prevented altogether.

We have now still in solution, magnesia and the alkalies; the simple detection of magnesia may be effected by means of phosphate of soda and ammonia; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesia is based upon the insolubility of magnesia in the pure state. The substance under examination is accordingly ignited in order to expel the ammoniacal salts, and the magnesia is then precipitated by means of barytes, the alkalies, the new-formed salt of barytes, and the excess of the caustic barytes added remaining in solution. By the addition of carbonate of ammonia the whole of the barytes is removed from the solution which contains now the fixed alkalies, the ammoniacal salt formed, and the excess of the carbonate of ammonia added.

The ammoniacal salts are then removed by evaporating the solution to dryness and igniting the residue; the ignited residue consists of the fixed alkalies alone. This method of separating the barytes has this advantage over that of effecting the removal of this earth by means of sulphuric acid, that the alkalies are obtained in the most convenient form for their subsequent individual detection and isolation, viz. as chlorides.

The detection of the ammonia requires, of course, a fresh sample of the substance under examination.

b. DETECTION OF THE ACIDS.

Before passing over to the examination for acids and electronegative substances, the analyst has to consider, in the first place, the nature of the detected bases and the class to which the substance under examination belongs with respect to its solubility in water or acids, since he may infer from these considerations which of the acids and electro-negative bodies *may*, and *which cannot* be present, and may thus save himself the trouble of making unnecessary experiments. I refer the student upon this point to the table which will be found in the appendix, and in which the various compounds are arranged according to their several degrees of solubility in water and acids. The general reagents applied for the detection of the acids are, for the inorganic acids, CHLORIDE OF BARIUM and NITRATE OF SILVER for the organic acids; CHLORIDE OF CALCIUM and PERCHLORIDE OF IRON. It is therefore indispensable that the analyst should first assure himself whether he has to operate upon a substance containing inorganic acids alone, or organic acids alone, or both together. In the examination for bases, the general reagents serve to effect the actual separation of the several groups of bases from one another; but in the examination for acids, they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids in combination with soda, for instance.

Barytes forms insoluble compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boracic acid, chromic acid, oxalic acid, tartaric acid, and citric acid; these compounds are soluble in hydrochloric acid, with the exception of sulphate of barytes. If therefore to a portion of a neutral solution, we add

1. *Chloride of barium*,

the formation of a precipitate will at once reveal the presence of at least one of these acids. Upon treating the precipitate formed with hydrochloric acid, the presence of sulphuric acid will become manifest, since all the salts of barytes are soluble in this menstruum, with the exception of the sulphate. When sulphate of barytes is present, the reaction with chloride of barium fails to effect the positive detection of the whole of the other acids enumerated. For upon filtering the hydrochloric solution of the precipitates and supersaturating the filtrate subsequently with ammonia, the borate, tartrate, citrate, &c. of barytes do not precipitate again, being kept in solution by the sal ammoniac formed. Chloride of barium, therefore, cannot serve to effect the actual separation of the several acids from one another, and is therefore of no use for their individual detection, except for sulphuric acid. It is, however, of great importance as a reagent, since the non-formation of a precipitate in neutral or alkaline solutions, upon its application, proves at once the absence of a considerable number of acids.

Silver forms compounds insoluble in water, with chlorine, iodine, bromine, and cyanogen; and the oxide of silver, with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid. The whole of these compounds are soluble in ammonia, with the solitary exception of iodide of silver, and in nitric acid, with the exception of iodide, chloride, bromide, and cyanide of silver. If, therefore, we add to our solution which, for the reason just now stated, must be perfectly neutral,

2. *Nitrate of silver,*

the ensuing precipitation reveals at once the presence of one or several of the acids enumerated; chromic acid, arsenic acid, and several other acids, of which the silver salts are colored, may even be individually recognized with a certain degree of safety, from the color of the precipitate. Upon treating the precipitate with nitric acid, the presence of the haloid compounds becomes manifest, since these remain undissolved, whilst the whole of the salts of the oxide dissolve. Nitrate of silver fails to effect the complete separation of those acids which form insoluble compounds with oxide of silver, for the same cause which renders the separation of acids by chloride of barium uncertain, viz. the ammoniacal salt formed prevents the reprecipitation by ammonia, of several of the salts of silver, from the acid solution. Nitrate of silver, besides effecting the separation of chlorine, iodine, bromine, and cyanagen, and indicating the presence of chromic acid, &c., serves also like the chloride of barium, to demonstrate at once the absence of a great many acids from neutral solutions which it fails to precipitate. The deportment which the solution under examination exhibits with chloride of barium and with nitrate of silver indicates, therefore, at once the further course of the investigation. Thus, for instance, if chloride of barium has produced a precipitate, whilst nitrate of silver has failed to do so, it is not necessary to test for phosphoric acid, chromic acid, boracic acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, provided always the solution contains no ammoniacal salts. The same is the case if we obtain a precipitate by nitrate of silver, but none by chloride of barium. Returning to our first supposition, viz., that the whole of the acids are present in the solution under examination, we have now detected CHLORINE, BROMINE, IODINE, and CYANOGEN, (for the separation and individual detection of these substances, I refer to § 101. Additions and remarks,) and likewise SULPHURIC ACID, and we have reason to test for all the other acids precipitated by these two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained in the course of the present work: the same remark applies to the rest of the inorganic acids, and thus to nitric acid and chloric acid.

Of the organic acids, oxalic acid, tartaric acid,* and paratartaric acid, are precipitated by chloride of calcium, from aqueous neutral solutions, in the cold, even though sal ammoniac be present; but the precipitation of citrate of lime is prevented by the presence of ammoniacal salts, and ensues only upon ebullition or mixing the solution with alcohol; alcohol serves also to effect the separation of malate of lime from aqueous solutions. Accordingly upon adding to our solution,

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* The tartrate of lime separates only after the lapse of some time.

3. *Chloride of calcium* and sal ammoniac,

OXALIC ACID, TARTARIC ACID, and PARATARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, (phosphate of lime for instance,) precipitate conjointly with the lime-salts of the organic acids. We must therefore select, for the individual detection of the precipitated organic acids, such reactions only as do not admit the possibility of confounding the organic with the inorganic acids which have likewise precipitated. For the detection of oxalic acid we select solution of gypsum in conjunction with acetic acid (§ 99. *c.* 5.); to effect the detection of tartaric and paratartaric acid, we treat the precipitate produced by chloride of calcium with solution of potass, since the lime-salt of these two acids alone are soluble in this menstruum, in the cold, whilst the whole of the other insoluble lime-salts remain undissolved.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID and MALIC ACID precipitate upon addition of alcohol to the fluid filtered off from the oxalate, tartrate, &c., of lime, and which contains still an excess of chloride of calcium. Sulphate and borate of lime precipitate invariably conjointly with the malate and citrate of lime, if sulphuric acid and boracic acid happen to be present; we must therefore carefully guard against confounding the lime precipitates of these acids with those of citric acid and malic acid. The alcohol is now removed by evaporation, and

4. *Perchloride of iron*

added. This reagent precipitates SUCCINIC ACID and BENZOIC ACID in combination with peroxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several groups from one another, and the individual detection of the various acids, have been fully described and explained in the former part of this work.

B. SPECIAL REMARKS AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

To § 117.

At the commencement of § 117, the analyst is directed to mix neutral or acid aqueous solutions with hydrochloric acid. This acid is to be added drop by drop. If no precipitate forms, a few drops are sufficient, since the only object in that case is, to acidify the fluid, in order to prevent the subsequent precipitation of the metals of the iron group, by sulphuretted hydrogen; if a precipitate is formed, the addition of the hydrochloric acid is to be continued until the precipitate ceases to increase, and the fluid has acquired a distinctly acid reaction. Instead of this course of proceeding, some chemists have proposed to acidify a fresh sample of the solution under examination, with nitric acid. However, disregarding even the fact that nitric acid likewise produces precipitates in many cases, (in solution of tartar emetic, for instance), I prefer the use of the hydrochloric acid, and this for the following reasons:—1. Metals are more readily precipitated by sulphuretted hydrogen, from solutions acidified with hydrochloric acid, than from solutions acidified with nitric acid;—2. In cases where the solution contains silver, protoxide of mercury, or lead, the further analysis is materially facilitated by the total or partial precipitation of these three metals in the form of chloride ;—and 3. This form is the best adapted for the individual detection of these three metals when present conjointly in the same solution. Besides, the application of the hydrochloric acid saves the necessity of examining whether mercury, which may be subsequently detected conjointly with the other metals of the fifth group, was originally present in the form of peroxide or in that of protoxide. That the analyst obtains part of the lead in the form of a chloride, and the rest subsequently in the precipitate produced by sulphuretted hydrogen in the acidified solution, can hardly be thought to militate against the application of this method, since he may, of course, omit the further examination for lead, if he detects this metal in the precipitate produced by the hydrochloric acid.

A basic salt, of antimony, for instance, may be separated by the hydrochloric acid from tartar emetic, or some other analogous compound, and precipitate in conjunction with the insoluble chloride of silver and mercury, and the sparingly soluble chloride of lead. This precipitate, however, redissolves readily in the excess of the hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the acidified fluid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated protochloride of mercury into bichloride. Should bismuth or chloride of antimony be present, the addition of the water, used to wash the precipitate produced by the hydrochloric acid, to the first filtrate, causes turbidity if the amount of free hydrochloric acid present is not sufficiently copious to prevent the separation of the basic salt. This turbidity exercises, however, no influence upon the further process, since sulphuretted hydrogen as readily converts these finely-divided precipitates into sulphurets, as if the metals were in actual solution. In the case of alkaline solutions, the addition of the hydrochloric acid is to be continued until the fluid acquires a strongly acid reaction. The hydrochloric acid neutralizes the substance which causes the alkaline reaction of the fluid, and the bodies which may be dissolved in it, and combined with it, separate. If the alkali was present in a free state, oxide of zinc, for instance, or alumina, &c., may precipitate. But these oxides redissolve in an excess of the hydrochloric acid; the chloride of silver, on the contrary, would not redissolve, and chloride of lead only with difficulty. If a metallic sulphur salt happen to be the cause of the alkaline reaction, the electro-negative sulphuret (e. g. sulphuret of antimony) precipitates upon the addition of the hydrochloric acid; whilst the electro-positive sulphuret (e. g. sulphuret of sodium) transposes with the constituents of hydrochloric acid to chloride of sodium and sulphuretted hydrogen. If an alkaline carbonate, or a cyanide or an alkaline sulphuret, happen to be the cause of the alkaline reaction, carbonic acid, hydrocyanic acid, or sulphuretted hydrogen escape. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of certain groups of bodies.

To § 118.

I have already had occasion to remark, that upon adding a reagent (e. g. sulphuretted hydrogen) to a fluid under examination, precipitation *may* or may *not* ensue. The precipitate produced, (by sulphuretted hydrogen, for instance,) may be *white*, or *yellow*, or *orange*, or *brown*, or *black*. Every one of these several cases is a different answer returned to the question which the analyst has put by means of the reagent, and every one of these replies has a different meaning. Correct observation and accurate apprehension and respective distinction of the several cases, is, therefore, indispensable. Any mistake in this respect leads to fallacious results.

The color of the precipitate is almost invariably pointed out as a criterion in the systematic course of analysis. We may presume that a darker precipitate will sometimes conceal one of a lighter color, e. g. that a precipitate of black sulphuret of mercury may conceal from view a precipitate of yellow sulphuret of arsenic; and on the other hand, we may conclude, that a light-colored precipitate cannot hide one of darker hue, and thus, for instance, that a white precipitate cannot conceal a black one. Conclusions of this kind cannot, however, always be drawn with the same degree of positive certainty, since few colors offer the pointed contrast of black and white, and many of them rather merge into each other, e. g. yellow and orange. In all cases where the indications afforded by the color of a precipitate are at all doubtful, it is advisable to pursue that course which the darker of the colors in question indicates, since this course comprises the whole of the metals which can possibly have precipitated, whilst the other course excludes the precipitates of darker color. The most comprehensive course is invariably the best, although it may be the most protracted and circuitous.

A judicious distribution and economy of time is especially to be studied in the practice of analysis; many of the operations may be carried on simultaneously, which the student will readily perceive and arrange for himself.

In cases where the analyst has to deal simply with metallic oxides of the sixth group, (e. g. oxide of antimony,) and of the fourth group, (e. g. the oxides of iron,) he need not precipitate the acidified solution with sulphuretted hydrogen, but may at once add hydrosulphuret of ammonia in excess to the neutralized solution. The sulphuret of iron, &c., will in that case precipitate, whilst the antimony, &c., will remain in the solution, from which they will, upon subsequent addition of an acid, at once precipitate as sulphuret of antimony, &c. This method has the advantage of rendering the fluid less dilute than is the case when sulphuretted hydrogen is used, and moreover of facilitating and accelerating the operation. I must, finally, remind the student once more, that the perfect purity of the reagents and the application in correct quantity, rank amongst the most indispensable conditions of successful analysis. This applies more particularly to sulphuretted hydrogen, especially when applied in the gaseous form. Students in such cases, often lose sight of the circumstance that sulphuretted hydrogen gas fails to precipitate highly acid solutions unless they be previously diluted with water.

To § 119.

The digestion of the precipitates from acid solutions which sulphuretted hydrogen has thrown down, requires above all that the digesting agent, (the hydrosulphuret of ammonia) be applied in correct proportion. A small quantity is generally sufficient, but should protosulphuret of tin be present, a somewhat larger amount is required. Inexperienced students, however, use frequently so much of it that, upon the subsequent addition of an acid, sulphur separates to such an amount that the color of the precipitated, electro-negative sulphuret, is quite obscured and concealed by it. The separation and individual detection of antimony, tin, and arsenic, is not a very easy task, if these three metals have been precipitated conjointly as sulphurets. Inexperienced students will find it difficult to distinguish between these before the blow-pipe. Of the many methods that may serve to distinguish between antimony, tin, and arsenic, when present conjointly as sulphurets, that given at § 119 has been proved the safest by experience. If sulphuret of arsenic, sulphuret of antimony, and sulphuret of tin, are deflagrated with an excess of nitrate of potass and carbonate of soda, the metals and the sulphur oxidize at the expense of the oxygen of the nitric acid: the fused mass contains accordingly alkaline arseniate, antimoniate, sulphate, and stannate, besides the excess of nitre and carbonate of soda. Upon treating the mass with water, the alkaline sulphate and arseniate are dissolved; the alkaline antimoniate is decomposed in such a manner, that an insoluble acid salt remains, whilst a small amount of antimonic acid dissolves in the form of a basic salt. A portion of the peroxide of tin also dissolves in the alkaline carbonate present. If boiling water is used, the amount of the dissolved antimonic acid and peroxide of tin is not inconsiderable, whilst it is only very minute if cold water is used; the latter is therefore preferable in this operation to boiling water. If the alkaline solution obtained is now saturated with nitric acid, and heat applied, the dissolved peroxide of tin and antimonic acid precipitate; this precipitate, however, is never free from admixture of arsenic. This will show how carefully the analyst ought to avoid getting much peroxide of tin or antimonic acid in solution. The neutral or slightly acidified fluid, which is filtered off from the precipitate, contains now still alkaline arseniate and sulphate. § 119 directs one portion of this filtrate to be tested with solution of nitrate of silver in conjunction with ammonia, and another portion with solution of acetate of lead. Since the fluid must be perfectly neutral to render the arseniate of silver visible, and since it is not always easy to hit upon the exact neutralization point, the fluid, as stated at § 119 is, after the addition of the solution of nitrate of silver, covered with a layer of dilute ammonia. This is the most efficient method of producing a precipitate when but small quantities of arsenic are present. Upon precipitating with solution of acetate of lead a mixture of sulphate and arseniate of lead is obtained. The presence of the sulphate of lead increases the bulk of the precipitate, and thus renders its collection and subsequent examination before the blow-pipe a task of greater facility than would be the case with the simple arseniate of lead; it increases moreover the bulk of the button. Although these reactions may be considered fully to demonstrate the presence of arsenic, yet the production of an arsenical mirror is, after all, the only conclusive proof of the presence of that metal.

The residue of tin and antimony which remains upon treating the deflagrated mass with water, must be thoroughly washed, and thus freed from every particle of nitrate of potass adhering to it, before it can safely be fused with cyanide of potassium; otherwise explosions will take place, (§ 102. *a.* 4.) which may not simply scatter the sample, but hurt the operator himself.

To § 120.

Upon heating the sulphurets of the second section of the fifth group to ebullition with nitric acid, lead, bismuth, copper, and cadmium, oxidize at the expense of a portion of the nitric acid, which is resolved into nitric oxide and oxygen; the sulphur separates, and the new-formed oxides combine with another portion of the nitric acid to soluble nitrates. Sulphuret of mercury, on the other hand, is not decomposed by nitric acid, unless a chloride be present, owing to imperfect washing. Ammonia decomposes the whole of the dissolved metallic nitrates. But the oxides of lead and bismuth are insoluble in the excess of ammonia, whilst those of cadmium and copper dissolve in an excess of this reagent. Ammonia affords us, therefore, a means both of testing the solution for the oxides of lead and bismuth, and of removing these oxides from it. The presence of oxide of copper is also indicated by this reagent, the ammonio-nitrate of copper, which forms upon its addition, imparting a blue color to the fluid under examination. The method of distinguishing between the lead, bismuth, copper, and cadmium, and effecting the separation of these four metals from one another, have already been sufficiently described and explained at § 92. (recapitulation and remarks.) With regard to the detection of bismuth, I have to observe, that this miscarries invariably if the excess of acid present is at all notable. The best way of limiting the excess of the acid to the lowest possible amount, is that described at § 120. But if the analyst contents himself with evaporating only *nearly* to dryness, so much free acid remains frequently that the separation of a basic salt cannot be accomplished.

Besides the methods given at § 92, (recapitulation and remarks,) and at § 120, to distinguish between cadmium, copper, lead, and bismuth, the following method yields very satisfactory results. Carbonate of potass is added to the nitric acid solution as long as a precipitate continues to form; solution of cyanide of potassium in excess is then added, and heat applied. This effects the complete separation of lead and bismuth in the form of carbonates, whilst copper and cadmium are obtained in solution as the double cyanides of copper and potassium, and cadmium and potassium. Lead and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in cyanide of potassium, sulphuretted hydrogen in excess, applying heat; and adding subsequently some more cyanide of potassium, in order to redissolve the sulphuret of copper, which may have precipitated conjointly with the sulphuret of cadmium. A yellow precipitate (sulphuret of cadmium) which is insoluble in cyanide of potassium, demonstrates the presence of cadmium. The fluid is filtered off from this precipitate, and hydrochloric acid subsequently added to the filtrate; when the formation of a black precipitate (sulphuret of copper) will demonstrate the presence of copper. The presence of mercury might indeed be considered sufficiently demonstrated by the black residue which remains upon treating the sulphuret with nitric acid. The eliminated sulphur, however, envelops frequently small particles of the other black sulphurets, and appear for this reason black here and there, and in some instances also heavy, from a mixture of sulphate of lead, (formed by the action of the nitric acid upon the sulphuret of lead). It is therefore indispensable to subject every residue remaining upon ebullition with nitric acid to further examination, unless the residue consists of pure yellow sulphur, which mostly floats upon the fluid. The test with clean copper is most convenient and expeditious. I have to remark, however, that the application of this test gives more frequently rise to fallacious results than the reaction with protochloride of tin. With regard to the latter, it is indispensable that the reagent be pure, and that the solution of mercury contain no longer any nitric acid If the protoxide of mercury has been separated first by hydrochloric acid, the precipitate of sulphuret of mercury which forms upon the addition of sulphuretted hydrogen, corresponds invariably to the peroxide, perchloride, &c. of mercury. If the analyst has to deal with an aqueous solution, or with a solution in very dilute hydrochloric acid, he has to consider that the mercury was originally present in the analysed substance, in the form of peroxide, perchloride, &c.: but in the case of a nitric acid solution, the mercury may have originally existed as protoxide, and subsequently acquired a higher degree of oxidation.

To § 121.

The precipitate produced by hydrosulphuret of ammonia may, as already stated, consist of sulphurets, of oxides, and of the phosphates of the alkaline earths, phosphate of alumina, oxalate of lime, (barytes and strontia). The borates of the alkaline earths and the oxalate of magnesia would, also, precipitate, were they not retained in solution by the sal ammoniac formed in the fluid or added to it. It is a matter of perfect indifference, as regards the final results of this operation, whether a precipitate forms or not, upon the simple addition of ammonia, since hydrosulphuret of ammonia decomposes the recently precipitated hydrated oxides of iron, &c. without difficulty. Nor can any positive inference respecting the presence or absence of certain metals and compounds be drawn from this reaction, unless the sulphuretted hydrogen were previously altogether removed from the fluid, which would be an unnecessary waste of time. Upon dissolving the precipitate in hydrochloric acid, or in aqua regia, the metallic sulphurets and the hydrated oxides are converted into soluble chlorides, whilst the phosphates and oxalates dissolve apparently without decomposition. If to this acid solution ammonia is added, the phosphates and oxalates are re-precipitated, and, conjointly with them, alumina, oxide of chromium, and peroxide of iron fall down, since these oxides do not (like the oxides of manganese, nickel, cobalt, and zinc) form soluble double compounds with ammoniacal salts. This precipitation by ammonia, in presence of sal ammoniac, may serve to effect the separation and individual detection of the whole of the enumerated substances. I myself pursued this method formerly; but I have abandoned it now, since in cases where comparatively small quantities only of zinc, cobalt, nickel, and manganese happen to be present, the oxides of these metals are liable to precipitate wholly in conjunction with peroxide of iron or alumina, and thus to escape detection. In § 121. we have two distinct cases, of which the first (*formation of a* WHITE *precipitate*) requires no further explanation, especially as it is included in the second, (*formation of a* DARK COLOURED *precipitate*). The second case is again arranged under two heads, according to the respective presence or absence of phosphates or of oxalates of the alkaline earths. For the latter compounds the still slightly acid solution is tested with perchloride of iron, chloride of calcium, and acetate of potass. The concurrent application of these reagents forms, as will be seen at a glance, a double test for both phosphoric and oxalic acid. The principle of the examination for phosphoric acid has been explained already at § 99. *a.* The principle whereon the examination for the oxalic acid is based is this :—Upon addition of acetate of potass to the hydrochloric acid solution of oxalate of lime, chloride of potassium is formed and acetic acid liberated; the acetic acid being unable to keep the oxalate of lime in solution, this salt precipitates.

The principle of the method described in case *a.*, to effect the individual detection of the metals of the third and fourth group, is exceedingly simple. It is based upon the separation of the alumina and oxides of zinc, which are soluble in boiling potass ley, from the oxide of iron, manganese, nickel, cobalt, and chromium, which are insoluble in that menstruum. For the subsequent separation and individual detection of the latter oxides, I refer to §§ 88. and 89.

The presumption in case *b.* is, that the presence of the phosphates or oxalates of the alkaline earths might interfere with these individual detections. The student is therefore instructed, in that place, to shake the fluid in the first place with carbonate of lime ; this effects the neutralization of the free acid, which maintains the oxalates and phosphates of the alkaline earths in solution, and consequently the precipitation of these salts. This operation effects, moreover, the precipitation of the peroxide of iron, which may be present in the solution, since this oxide is insoluble in perfectly neutral fluids. It will be readily seen that this method of removing the peroxide of iron may be advantageously resorted to in cases where the presence of a certain amount of that oxide might interfere with the detection of the manganese, nickel, and cobalt.

The method of examining for oxalic acid, which is given at § 121. 2. *b. α.*, and based upon the circumstance that, when oxalic acid ($C_2\ O_3$) comes into contact with peroxide of manganese ($Mn\ O_2$) and free acid, (sulphuric acid,) protosulphate of manganese is formed, whilst the liberated equivalent of oxygen combines with the constitutents of the oxalic acid, to two equivalents of carbonic acid, ($Mn\ O_2 + SO_3 + C_2\ O_3) = (Mn\ O,\ SO_3 + 2\ CO_2$.) The decomposition of the oxalic acid in § 121. 2. *b. α. ββ.* rests upon the same principle.

To § 130.

The third class of substances has no strictly definable limits, as the solubility or insolubility of several compounds belonging to it depends very much upon the quantity and concentration of the acid and the time of boiling. Besides the difficultly soluble substances enumerated, the analyst has to look particularly for many metallic sulphurets and iodides, which dissolve equally only upon continued boiling in concentrated hydrochloric acid. If a substance dissolves in nitric acid, upon long protracted ebullition, the analyst must not conclude from this, that protochloride of mercury is absent, since this substance, as I have already stated, is converted in this process into pernitrate of mercury and perchloride of mercury, and is thus dissolved.

Chloride of silver, protochloride of mercury, and chloride of lead may have been present in the original compound in the form of chloride, or may have been converted into this form by the hydrochloric acid. The presence of the chloride of lead has in that case been detected already in the aqueous solution. Whether the two other chlorides were originally present in that form, may be ascertained in the following manner:—The substance insoluble in water is treated with dilute nitric acid. This effects the solution of the whole of the salts of protoxide of mercury and oxide of silver, whilst the above enumerated chlorides and the iodide of silver remain undissolved. These are then separated by means of ammonia, which serves at the same time to effect the detection of the protochloride of mercury.

The decomposition of the sulphates of the alkaline earths may be effected also in the humid way by protracted boiling with solution of carbonate of potass. But the fusion with carbonate of potass and soda, yields far safer results, and is moreover very expeditious when operating upon small quantities. This method has besides this advantage over the decomposition in the humid way that it leads to the positive detection of the presence of silicic acid.

The sulphates of the alkaline earths are decomposed by the alkaline carbonates in such a manner that carbonates of the alkaline earths and sulphate of the alkali are formed. If the precipitate of the former be not thoroughly washed, previously to its solution in hydrochloric acid, sulphates of the alkaline earths will again be formed by the action of the sulphated alkali which still adheres to the precipitate; this would tend to vitiate the results of the experiment, since, for instance, all the barytes dissolved might reprecipitate.

Carbon has been connected with this third class, since it occurs sometimes in the course of the examination, and may thus become a great obstacle to the progress of the inexperienced student, should he be unprepared for its presence. Graphite is distinguished from the other forms of carbon by its difficult combustion before the blow-pipe, and its non-combustion in a platinum spoon; besides these indications, the iron, which graphite generally contains in admixture, denotes its presence.

To § 131.

The analysis of cyanogen compounds is not very easy in certain cases, and sometimes it is indeed extremely difficult to ascertain even whether we have really a cyanide before us or not. If, however, the phenomena which the substance under examination manifests upon ignition, (§ 107. A. 1. 2.) be carefully observed, and also, whether upon ebullition with hydrochloric acid any odor of hydrocyanic acid is emitted, (§ 109. A. 2.) the presence or absence of a cyanide will not long remain a matter of doubt.

It must now above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two quite different classes. They are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN, or with some other analogous compound radical.

All the simple cyanides are decomposed upon boiling with concentrated hydrochloric acid, into metallic chlorides and hydrocyanic acid. Consequently their analysis, is never difficult. The ferrocyanides, &c., however, (to which the method described at § 131. refers indeed exclusively,) undergo by acids such complicated decompositions that their analysis in this manner is a task not so easily accomplished. Their decomposition by potass is far more simple. The potass yields its oxygen to the metal combined with the ferrocyanogen, &c., the oxide precipitates, and the reduced potassium forms soluble ferrocyanide, &c. of potassium with the liberated radical. But several oxides are soluble in an excess of caustic potass, such as oxide of lead, oxide of zinc, &c. If, therefore, the double ferrocyanide of zinc and potassium, for instance, be boiled with caustic potash, it will completely dissolve in that menstruum.

Were we to add an acid to this solution, we should simply reobtain our original precipitate of the double ferrocyanide of zinc and potassium, and our experiment would consequently be of no avail. To prevent this, we transmit sulphuretted hydrogen through the solution. This converts the whole of the heavy metals which the potass contains in solution as oxides, into sulphurets. Those sulphurets which are insoluble in potass, such as sulphuret of lead, sulphuret of zinc, &c., precipitate, whilst those which are soluble in alkaline sulphurets, such as sulphuret of tin, sulphuret of antimony, &c., remain in solution ; these latter also precipitate subsequently, upon the addition of an acid.

The fluid filtered off from the precipitated oxides or sulphurets, contains the cyanogen invariably as ferrocyanide, &c., of potassium, (provided, of course, the analysed compound consist really of a double ferrocyanide, &c., &c.) From most of the compounds (ferrocyanide, ferricyanide, chromicyanide, and manganocyanide of potassium) the cyanogen separates partly as hydrocyanic acid, upon boiling the solution with sulphuric acid, and may thus be readily detected. But the cobalticyanide of potassium is not decomposed by sulphuric acid, and this renders the *direct* demonstration of the presence of cyanogen in this double compound a difficult task. Upon fusion with nitrate of potass, the whole of these double compounds suffer decomposition, cobalticyanide of potassium not excepted. The reason why the fusion of these double compounds with nitrate of potass is to be preceded by evaporation with an excess of nitric acid, is simply to prevent the occurrence of explosion. Caution is highly advisable in this operation. If the analyst wishes simply to detect the bases in simple or double cyanides, he may in most cases accomplish his object by igniting the substance under examination, or by fusing it in conjunction with carbonate of soda and potass. This process yields the metals either in the metallic state, or in combination with carbon. If the compound has been fused with the alkaline carbonates, cyanide of potassium is found in the slag, should this not have been converted into cyanate of potass, owing to the adventitious presence of reducible oxides. (Vide § 101. *d*. 2.)

APPENDIX.

I.

§ 134.

DEPORTMENT OF THE MOST IMPORTANT OF THE ALKALOIDS (VEGETO-ALKALIES) WITH REAGENTS.

A SYSTEMATIC METHOD OF EFFECTING THE DETECTION OF THESE SUBSTANCES.

The detection, and separation, of the alkaloids is a task of far greater difficulty than that of most of the inorganic bases. Although the difficulty of this task is owing partly to the circumstances that scarcely one of the compounds which the alkaloids form with other substances, is perfectly insoluble or particularly characterized by its color or any other salient property, yet the principal cause of this difficulty must be ascribed to the want of accurate and minute investigations of the salts and other compounds of the alkaloids, and of the products of their decomposition. This is the reason why we are able only to apprehend the manifestation of the reactions, but unable to conceive the causes of these reactions, and consequently to understand the conditions which may tend to modify them.

Now although, in the present imperfect state of our knowledge of the alkaloids, an attempt to define their deportment with reagents, and to base thereon a method of effecting their separation or, at least, individual detection, must of necessity fall very short of perfection, yet, having made a great many experiments on the nature and deportment of these substances, I will attempt here, for the benefit of young chemists, and more particularly pharmaceutists, to describe in some measure the reactions which the most important of the vegeto-alkalies manifest with other bodies, and to lay down a systematic method of effecting the individual detection of these alkaloids.

The classification of the vegeto-alkalies into groups which I have adopted here, is based upon their deportment with certain general reagents. I have verified by numerous experiments the whole of the reactions described in the succeeding paragraphs.

FIRST GROUP.

§ 135.

VEGETO-ALKALIES WHICH ARE PRECIPITATED BY POTASS FROM THE SOLUTIONS OF THEIR SALTS, AND REDISSOLVE SUBSEQUENTLY IN AN EXCESS OF THE PRECIPITANT. Of the vegeto-alkalies of which I purpose to treat, *one* only belongs to this group, viz.,

MORPHINE ($C_{35}\ H_{20}\ N\ O_6 = \overset{+}{Mo}$)

1. Morphine appears usually in the form of colorless, brilliant, four-sided prisms or, upon precipitation from the solution of its salts, as a white powder composed of crystalline flakes. It has a bitter taste, and dissolves very sparingly in cold, but somewhat more readily in boiling water. Of cold alcohol, it requires ninety parts by weight for solution; of boiling alcohol, from twenty to thirty parts. The solutions of morphine in alcohol and hot water manifest distinctly alkaline reactions. This alkaloid is insoluble in ether.

2. Morphine neutralizes acids completely, and forms with them the SALTS OF MORPHINE. These salts are readily soluble in water and spirits of wine, but are insoluble in ether; their taste is bitter and disagreeable. Most of them are crystallizable.

3. *Potass* and *ammonia* precipitate morphine from the solutions

of its salts, in the form of a white crystalline powder. Stirring and friction on the sides of the vessel promote the separation of the precipitate, which redissolves with great readiness in an excess of the potass, but with somewhat more difficulty in ammonia. The precipitated morphine dissolves also in chloride of ammonium and also, but with difficulty, in carbonate of ammonia.

4. *Carbonate of potass* and *carbonate of soda* produce the same precipitate as potass and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkaline bicarbonate is added to a solution of morphine in caustic potass, the morphine separates (especially after previous ebullition) in the form of a crystalline powder. A more minute inspection, especially through a magnifying glass, shews this powder to consist of small acicular crystals; seen through a glass which magnifies one hundred times, these crystals present the form of four sided prisms.

5. *Bicarbonate of soda* and *bicarbonate of potass* precipitate morphine from the solutions of its neutral salts, in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of salts of morphine, in the cold.

6. The action of strong *nitric acid,* upon morphine or one of its salts, in the solid state or in concentrated solutions, produces a fluid varying from red to yellowish red. Dilute solutions do not change their color, upon addition of nitric acid, in the cold, but upon boiling they acquire a yellow tint.

7. *Neutral perchloride of iron* imparts a beautiful dark blue tint to neutral solutions of salts of morphine. This tint disappears upon the addition of an acid. Should the solution contain admixture of animal or vegetable extractive matters, or of acetates, the coloration will appear clouded and less distinct.

8. If *iodic acid* is added to a solution of morphine or of a salt of morphia, IODINE separates. In aqueous and concentrated solutions, the separated iodine appears as a kermes brown precipitate, whilst in alcoholic and dilute solutions it imparts a brown or

yellowish-brown color to the fluid. The addition of starch paste to the fluid heightens the delicacy of the reactions considerably, since the blue tint of the iodide of starch remains perceptible still in exceedingly dilute solutions, which is not the case with the brown coloration imparted by iodine.

9. *Perchloride of gold* produces in concentrated solutions of salts of morphine a flocculent yellowish grey brown precipitate which redissolves to a green fluid in an excess of the precipitant and likewise in hydrochloric acid. In dilute solutions the reagent produces simply a green coloration; but in either case the fluid acquires a yellow tint, after standing for some time, and metallic gold separates in the form of a yellowish brown powder.

Second group.

§ 136.

VEGETO-ALKALIES WHICH ARE PRECIPITATED BY POTASS FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE, TO A PERCEPTIBLE EXTENT, IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY BICARBONATE OF SODA EVEN FROM ACID SOLUTIONS: Narcotine—Quinine—Cinchonine.

a. NARCOTINE ($C_{46} H_{25} N O_{14} = \overset{+}{\text{Na}}$)

1. Narcotine appears usually in the form of colorless, brilliant, rhombic prisms, or, upon precipitation by alkalies, as a white loose crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but more readily upon heating. Solid narcotine is tasteless, but the alcohol and ethereal solutions are intensely bitter. Narcotine does not alter vegetable colors.

2. Narcotine dissolves readily in acids, combining with them and forming salts. These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even upon simple evaporation.

Most of the salts of narcotine are amorphous, and soluble in water, alcohol, and ether.

3. *Pure alkalies*, and *alkaline carbonates*, and *bicarbonates* precipitate narcotine from the solutions of its salts, in the form of a white powder, which seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitant. If a solution of narcotine is mixed with ammonia, and ether subsequently added, the narcotine which separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers.

4. *Concentrated nitric acid* dissolves narcotine to a colorless fluid which acquires a pure yellow tint upon application of heat.

5. *Concentrated sulphuric acid* dissolves narcotine to a yellow fluid which turns brown upon application of heat. A solution of narcotine in concentrated sulphuric acid containing a *slight* admixture of nitric acid, appears of an intense blood-red color, which disappears altogether upon the addition of a somewhat larger amount of nitric acid.

6. If narcotine or one of its salts is dissolved in an excess of dilute sulphuric acid, some finely levigated peroxide of manganese added, the mixture heated to boiling, and maintained in ebullition for the space of several minutes, the narcotine absorbs oxygen and is converted into opianic acid, cotarnine (a base soluble in water) and carbonic acid.

b. Quinine ($C_{20}\,H_{12}\,N\,O_2 = \overset{+}{\text{Ch}}$.)

1. Quinine appears either in the form of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble in cold, but somewhat more readily in hot water. It is readily soluble in spirits of wine, both cold and hot, but far less so in ether. The taste of quinine is intensely bitter; the solutions of quinine manifest alkaline reaction.

2. Quinine neutralizes acids completely. The salts taste intensely bitter; most of them are crystallizable, and for the greater part readily soluble in water and spirits of wine.

3. *Potass, ammonia,* and the simple *carbonates of the alkalies* produce in solutions of salts of quinine, (provided they be not too dilute) a white, loose, pulverulent precipitate of hydrated quinine, which immediately after precipitation, appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of aggregated crystalline needles. The precipitate redissolves to a hardly perceptible extent only, in an excess of potass, but more readily in ammonia. It is hardly more soluble in fixed alkaline carbonates than in pure water. If a solution of quinine is mixed with ammonia, and ether is subsequently added, and the mixture shaken, the quinine which separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers.

4. *Bicarbonate of soda* also produces, and this both in neutral and acid solutions of salts of quinine, a white pulverulent precipitate of hydrated quinine. From dilute solutions, the quinine separates only *after the lapse of some time,* and the precipitate appears in such cases in the form of white and opaque needles aggregated into tufts. Vigorous stirring of the fluid promotes the separation of the precipitate considerably. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more perfect, the less the excess of the precipitant. From this solution in an excess of bicarbonate of soda, the quinine precipitates upon protracted ebullition.*

5. *Concentrated nitric acid* dissolves quinine to a colorless fluid, which turns yellowish upon the application of heat.

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* A remark made by C. F. Oppermann (Considérations sur les Poisons Végétaux, Strasbourg, 1845) impeaching the correctness of my statement regarding the precipitation of a solution of quinine acidified with sulphuric acid by bicarbonate of soda, induced me to repeat my former experiments, but invariably with the same results, viz. concentrated solutions were precipitated immediately, dilute solutions after the lapse of from two to fifteen minutes, this operation being greatly promoted by vigorous stirring of the fluid.

6. *Concentrated sulphuric acid* likewise dissolves pure quinine and pure salts of quinine to colorless fluids which do not acquire any coloration upon being heated to the point of incipient evaporation of the sulphuric acid, but turn subsequently yellow and afterwards brown. Sulphuric acid containing an admixture of nitric acid, dissolves quinine to a colorless or faint yellowish fluid.

c. CINCHONINE ($C_{20}\,H_{12}\,N\,O = \overset{+}{Ci}.$)

1. Cinchonine appears either in the form of pellucid, brilliant, four-sided prisms, or of fine white crystalline needles, or finally, when precipitated from concentrated solutions, as a loose white powder. Recently prepared, or precipitated cinchonine is tasteless, but acquires subsequently the bitter taste of the bark. Cinchonine is nearly altogether insoluble in cold, and of exceedingly difficult solution in hot water; it is but little soluble in cold dilute spirits of wine, somewhat more readily in hot spirits of wine, and most readily in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonine separates upon cooling. Solutions of cinchonine taste bitter and manifest alkaline reaction. Cinchonine is insoluble in ether.

2. Cinchonine neutralizes acids completely. The salts have the bitter taste of the bark; most of them are crystallizable, and generally more readily soluble in water and spirits of wine, than the corresponding quinine compounds. Ether fails to dissolve them.

3. Cinchonine, when heated cautiously, fuses at first; subsequently white fumes arise, which like benzoic-acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate. This sublimation of cinchonine is attended with emission of a peculiar aromatic odor.

4. *Potass*, *ammonia*, and the *neutral carbonates of the alkalies* produce in solution of salts of cinchonine, a white, loose, precipitate of CINCHONINE, which does not exhibit a distinctly crystalline appearance even though viewed through a lens magnifying from

200 to 300 times. The precipitate does not redissolve in an excess of the precipitants.

5. *Bicarbonate of soda* and *bicarbonate of potass* precipitate cinchonine in the same form as at 4. both from neutral and acid solutions, but not so completely as the carbonates of the alkalies. The bicarbonates accordingly fail to precipitate highly dilute solutions, and the fluid filtered off from the precipitate produced in more concentrated solutions, turns turbid upon protracted boiling.

6. *Concentrated sulphuric acid* dissolves cinchonine to a colorless fluid which turns brown upon application of heat, and acquires finally a black color. Solution of cinchonine in concentrated sulphuric acid containing an admixture of nitric acid is equally colorless in the cold, but, upon application of heat, passes through the intermediate tints of yellow, red-brown, and brown, and turns finally black.

Recapitulation and Remarks.

The alkaloids of the second group are altered or precipitated by various other reagents besides those mentioned above; the reactions are, however, not adapted to effect their individual detection and separation. Thus, for instance, dilute solution of iodine produces in solutions of the salts of the three alkaloids belonging to this group, *red-brown* precipitate, bichloride of potassium, *yellowish-white,* perchloride of mercury, *white,* perchloride of gold, *yellow,* nitrate of silver, with addition of ammonia to neutralization, *white,* tincture of galls, *yellowish-white flocculent* precipitates, &c.

Narcotine and Quinine being soluble in ether, whilst cinchonine is insoluble in that menstruum, they may be most readily separated by this means from the latter alkaloids. To effect their separation, the analyst need simply mix the solution of the three alkaloids with ammonia in excess, add subsequently ether, and filter the solution of quinine and narcotine off from the undissolved cinchonine. If the ether be subsequently evaporated at a gentle heat, the ammonia being all the while maintained in excess, the narcotine will precipitate, and may be readily separated by filtration from the quinine which remains in solution. The quinine may then likewise be precipitated from the solution by cautious neutralization of the ammonia with an acid, and may finally be recognized under the microscope, by the form of its crystals.

THIRD GROUP.

§ 137.

VEGETO-ALKALIES WHICH ARE PRECIPITATED BY POTASS FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE NOT PRECIPITATED FROM ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALIES: Strychnine, Brucine, Veratrine.

a. STRYCHNINE ($C_{44} H_{24} N_2 O_4 = \overset{+}{Sr}$.)

1. Strychnine appears either in the form of white, brilliant, octohedrons, or of four-sided prisms, or finally, when produced by precipitation, or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is nearly altogether insoluble in cold, and scarcely soluble in hot water. It is insoluble in absolute alcohol and ether, and difficultly soluble in dilute spirits of wine.

2. Strychnine neutralizes acids completely. Most of the salts of strychnine are crystallizable and soluble in water. All the salts of strychnine have an insupportably bitter taste, and are exceedingly poisonous.

3. *Potass* and *carbonate of potass* produce in solutions of salts of strychnine white precipitates of strychnine, which are insoluble in an excess of the precipitants. Viewed through a lens, magnifying one hundred times, the precipitate appears as an

aggregate of small crystalline needles. From dilute solution the strychnine separates only after the lapse of some time, in form of crystalline needles, which are perfectly visible even to the naked eye.

4. *Ammonia* produces the same precipitate as potass. The precipitate redissolves in an excess of ammonia, but after a short time (or if the solution is highly dilute, after a more considerable lapse of time) the strychnine crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. *Bicarbonate of soda* produces, in neutral solution of salts of strychnine, a precipitate of strychnine, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline) the precipitate dissolves readily in the liberated carbonic acid. The addition of bicarbonate of soda to acid solution of strychnine, causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnine crystallizes from the fluid in distinct prisms, and this crystallization continues in proportion as the free carbonic acid escapes. If a concentrated solution of strychnine, supersaturated with bicarbonate of soda, is boiled for some time, a precipitate forms immediately; from dilute solution this precipitate separates only after concentration.

6. The addition of an aqueous solution of *iodic acid* to solutions of salts of strychnine, produces no alteration in the cold; but upon subsequent application of heat, the fluid turns VIOLET, and after the lapse of some time a blackish precipitate separates.

7. *Sulphocyanide of potassium* produces in concentrated solutions of salts of strychnine immediately, and in dilute solution, after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, and is but little soluble in an excess of the precipitant.

8. Upon mixing a drop of *concentrated sulphuric acid* containing about $\frac{1}{100}$ part of *nitric acid* in admixture, with a little

strychnine or salt of strychnine, upon a watch glass, solution ensues unattended with any peculiar reaction. But if a small grain of brown *peroxide of lead* be now added, the fluid will immediately acquire a blue tint, which turns soon afterwards violet, and changes gradually to green.

9. *Perchloride of mercury* produces, in solutions of salts of strychnine, a white precipitate, which changes after some time to crystalline needles aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution, the double compound re-crystallizes in distinct needles.

10. *Concentrated nitric acid* dissolves strychnine and its salts to colorless fluids, which become yellow upon the application of heat.

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b. BRUCINE ($C_{44}\ H_{25}\ N_2\ O_7 = Br.$)

1. Brucine appears either in the form of transparent, rhombic prisms, or in that of crystalline needles, aggregated into stars, or as a white powder composed of minute crystalline scales. Brucine is difficultly soluble in cold, but somewhat more readily so in hot water. Both absolute and dilute alcohol dissolve it readily, but it is insoluble in ether. Its taste is intensely bitter.

2. Brucine neutralizes acids completely. The salts of brucine are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potass* and *carbonate of potass* throw down from solutions of salts of brucine a white precipitate of brucine, which is insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, the precipitate appears to consist of very minute grains; but, upon further inspection, these grains are seen to form into needles, which latter arrange themselves subsequently into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces a whitish precipitate in solution of salts of brucine, which appears at first like a number of minute drops of

oil, but changes subsequently to small needles. The precipitate redissolves, immediately after separation, in an excess of the precipitant, but after a very short time (or, if the solution is highly dilute, after a more considerable lapse of time) the brucine crystallizes from the ammoniacal solution in small concentrically grouped needles, which addition of ammonia fails to redissolve.

5. *Bicarbonate of soda* produces, in neutral solutions of salts of brucine, a precipitate of brucine, which separates after the lapse of a short time, in form of concentrically aggregated needles of silky lustre, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare strychnine). Bicarbonate of soda fails to precipitate acid solutions of salts of brucine. But this alkaloid separates subsequently (after a considerable lapse of time, with the escape of carbonic acid) in regular and comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucine and its salts to intensely red fluids, which acquire subsequently a yellowish red tint, and become completely yellow upon the application of heat. Upon addition of protochloride of tin, or hydrosulphuret of ammonia, to this yellow fluid, (no matter whether concentrated or diluted with water,) the but little intense yellow colour changes to a most intense violet tint.

7. *Concentrated sulphuric acid* dissolves brucine to a faint rose-colored fluid.

8. The addition of iodic acid to solutions of salt of brucine produces no visible alteration in the cold, but, upon boiling, the fluid acquires a wine-red tint.

9. *Sulphocyanide of potassium* produces in concentrated solution of salts of brucine immediately, and in dilute solutions, after some time, a granular crystalline precipitate, which, when viewed under the microscope, appears composed of variously aggregated polyhedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Perchloride of mercury* produces also a white granular precipitate, which, when viewed under the microscope, appears composed of small round-shaped crystalline grains.

c. VERATRINE (formula not yet settled) $\overset{+}{\text{Ve}}$.

1. Veratrine appears generally as a pure white, or yellowish or greenish white powder, of acrid and burning (but not bitter) taste and exceedingly poisonous action. Veratrine acts with exceeding energy upon the membranes of the nose; even the most minute quantity of the powder excites the most violent sneezing. Veratrine is insoluble in water; it dissolves readily in alcohol, but more sparingly in ether. At a temperature as low as 122° it fuses like wax and solidifies subsequently, upon cooling, to a transparent yellow mass.

2. Veratrine neutralizes acids completely. Some salts of veratrine are crystallizable, others dry up into a gummy mass. They are soluble in water, and of acrid and burning taste.

3. *Potass, ammonia,* and the *simple carbonates of the alkalies* produce in solutions of salts of veratrine, a flocculent white precipitate, which viewed under the microscope, immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and small clusters of short prismatic crystals are observed here, and there, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potass and carbonate of potass. It is slightly soluble in ammonia, in the cold, but the dissolved portion separates again upon application of heat.

4. With *bicarbonate of soda* and *bicarbonate of potass,* veratrine comports itself like strychnine and brucine. It separates however readily, upon ebullition, even from dilute solutions,

5. If veratrine is acted upon with *concentrated nitric acid,* it agglutinates at first into small resinous lumps, which subsequently dissolve slowly in the acid. The solution presents a reddish yellow color of but little intensity.

6. When acted upon with *concentrated sulphuric acid,* veratrine agglutinates also into resinous lumps at first, but these lumps dissolve subsequently with great readiness to a faint yellow fluid, the color of which increases gradually in depth and in-

tensity, changes afterwards to a reddish yellow, then to an intense blood red, subsequently to crimson, and turns finally violet.

7. *Sulphocyanide of potassium* produces only in highly concentrated solutions of salts of veratrine flocculent gelatinous precipitates.

Recapitulation and Remarks.

The alkaloids of the third group are also precipitated by many other reagents besides those above mentioned, as, for instance, by tincture of galls, bichloride of platinum, &c. But the universality of these reactions render them of but little importance in an analytical point of view.

Strychnine may be separated from brucine and veratrine by means of absolute alcohol, since it is insoluble in that menstruum whilst the two latter alkaloids dissolve readily in it. The identity of strychnine is established best by the reaction with peroxide of lead and sulphuric acid, containing an admixture of nitric acid; and also by the form of its crystals viewed under the microscope, or finally by the form of the precipitate which sulphocyanide of potassium and perchloride of mercury produce in solutions of its salts. Brucine and veratrine are not readily separated from one another, but may be detected side by side. The identity of brucine is established best by the reactions with nitric acid and protochloride of tin, or hydrosulphuret of ammonia, or by the crystalline form of the precipitate which ammonia produces in solution of salts of brucine. Veratrine is sufficiently distinguished from brucine and the other alkaloids which we have treated of, by its characteristic deportment at a gentle heat, and also by the form of the precipitate which alkalies produce in solutions of its salts. To distinguish veratrine by the side of brucine, the reaction with sulphuric acid is employed.

To these alkaloids, I will add *salicine,* although this substance does not properly belong to the same class of chemical compounds with the vegeto-alkalies.

§ 138.

SALICINE ($C_{21} H_{12} O_9$.

1. Salicine appears either in form of white crystalline needles and scales of silky lustre, or, in cases where these crystals are very small, as a powder of silky lustre—it has a bitter taste. It is readily soluble in water and alcohol, but insoluble in ether.

2. No reagent precipitates salicine as such.

3. Salicine, when acted upon with *concentrated sulphuric acid*, agglutinates into lumps like resin, and acquires an intensely blood red color, but does not dissolve in the acid; the color of the latter remains unaltered.

4. If an aqueous solution of salicine is mixed with *hydrochloric acid or dilute sulphuric acid,* and the mixture boiled for a short time, the fluid turns suddenly turbid and deposits a fine granular crystalline precipitate (saliretine).

SYSTEMATIC COURSE LEADING TO THE DETECTION OF THE VEGETO-ALKALIES TREATED OF IN THE FOREGOING PARAGRAPHS, AND OF SALICINE.

§ 139.

The analytical course which I am now about to describe proceeds upon the supposition that the analyst has to examine a concentrated solution of one or several salts of the vegeto-alkalies, which solution is free from any admixture of substances which might tend to obscure or modify the reactions. For the modifications which the presence of coloring or extractive matter, &c. requires, I refer to § 142.

I. DETECTION OF THE VEGETO-ALKALIES AND OF SALICINE, IN SOLUTIONS SUPPOSED TO CONTAIN BUT ONE OF THESE SUBSTANCES.

§ 140.

1. Dilute potass ley is added drop by drop to a portion of the aqueous solution, until the fluid acquires a hardly perceptible alkaline reaction.

a. NO PRECIPITATE IS FORMED; this proves positively the total absence of the vegeto-alkalies, and indicates the presence of SALICINE. To set all doubt at rest on this point, the original solution is tested with concentrated sulphuric acid, and with hydrochloric acid, according to the directions of § 138. 3. and 4.

b. A PRECIPITATE IS FORMED. Potass is added drop by drop, until the fluid manifest a strongly alkaline reaction.

α. *The precipitate redissolves:* MORPHINE. To arrive at a positive conclusion on this point, another portion of the solution is tested with iodic acid, (§ 135. 8.), and a portion of the original substance with nitric acid, (§ 135. 6.)

β. *The precipitate remains undissolved:* Presence of a vegeto-alkali of the second or third group. Pass over to 2.

2. A second portion of the original solution is acidified with from two to three drops of dilute sulphuric acid, and a saturated solution of bicarbonate of soda subsequently added until the acid reaction is exactly neutralized; the sides of the vessel are then strongly rubbed, and the mixture allowed to stand at rest for half an hour.

a. NO PRECIPITATE IS FORMED: Absence of narcotine, quinine and cinchonine. Pass over to 3.

b. A PRECIPITATE IS FORMED: Narcotine, quinine, or cinchonine. A portion of the original solution is mixed with an excess of ammonia, a sufficient quantity of ether added, and the mixture shaken.

α. *The precipitate which forms at first upon the addition of the ammonia, redissolves in the ether and the clear fluid presents two distinct layers.* Narcotine or quinine. The test tube is placed in hot water to evaporate the ether, care being taken to maintain the ammonia in sufficient excess. If a precipitate separates, this is NARCOTINE. The reaction described at § 136. *a.* 5. may serve as a conclusive proof of the presence of this substance. If no precipitate separates, the analyst may conclude that QUININE is present. To set all doubt at rest on this point, the ammoniacal solution (which has been nearly evaporated to dryness) is very slightly acidified with one or two drops of acetic acid, and subsequently precipitated with carbonate of potass; the precipitate is then finally inspected under the microscope. (Compare § 136. *b.* 3.)

β. *The precipitate which forms upon the addition of ammonia does not redissolve in the ether:* CINCHONINE. The deportment of cinchonine when heated (the exhalation of a peculiar aromatic odor) may serve as a conclusive test (§ 136. *c.* 3.)

3. A portion of the original substance, or of the residue which will remain upon evaporating the solution, is placed into the hollow of a watch-glass, and treated with concentrated sulphuric acid.

a. A colorless solution is obtained which, upon application of heat, turns of a faint olive green: STRYCHNINE. The reaction with sulphuric acid containing nitric acid in admixture, and peroxide of lead is resorted to as a conclusive test, (§ 137. *a.* 8.)

b. A rose-colored solution is obtained which turns deep red upon addition of nitric acid: BRUCINE. The reaction with nitric acid and protochloride of tin is resorted to as a conclusive test, (§ 137. *b.* 6.)

c. A yellow solution is obtained, the color of which changes to a yellowish red, and subsequently to blood red, and turns afterwards crimson: VERATRINE.

II. DETECTION OF THE VEGETO-ALKALIES AND OF SILICINE IN SOLUTIONS, WHICH ARE SUPPOSED TO CONTAIN SEVERAL OR THE WHOLE OF THESE SUBSTANCES.

§ 141.

1. Dilute potass ley is dropped into a portion of the aqueous solution, until the fluid acquires a hardly perceptible alkaline reaction.

a. NO PRECIPITATE IS FORMED: This proves the total absence of vegeto-alkalies, and indicates the presence of SALICINE. The reactions with concentrated sulphuric acid and with hydrochloric acid are resorted to as conclusive tests. (Compare § 138. 3. and 4.)

b. A PRECIPITATE IS FORMED: Potass is added drop by drop until the fluid manifests a strongly alkaline reaction.

α. *The precipitate redissolves.* Absence of the vegeto-alkalies of the second and third group. Presence of MORPHINE. The reactions with iodic acid (§ 135. 8.) and with nitric acid (§ 135. 6.) are resorted to as conclusive tests. Examination for salicine, vide 4.

β. *The precipitate does not redissolve or at least not completely.* The fluid is filtered off from the precipitate, and the latter treated as directed at 2. The filtrate is mixed with the bicarbonate of soda or bicarbonate of potass, and the mixture heated to boiling and maintained in ebullition until evaporated nearly to dryness. The residue is treated with water. If it dissolves completely, this is a sign that no morphine is present; but if an insoluble residue remains, this indicates the presence of morphine. The reactions with iodic acid (§ 135. 8.) and with nitric acid (§ 135. 6.) are resorted to as conclusive tests.

2. The precipitate of 1. *b.* β. is washed with cold water and subsequently dissolved in a slight excess of dilute sulphuric acid; solution of bicarbonate of soda is added to the fluid until the acid

reaction is neutralized ; the mixture is stirred, the sides of the vessel being vigorously rubbed, and the fluid is then allowed to stand at rest for half an hour.

a. NO PRECIPITATE IS FORMED. Absence of narcotine, cinchonine, and quinine. The solution is heated to boiling and kept in ebullition until evaporated nearly to dryness. The residue is treated with cold water. If it dissolves completely, pass over to 4. ; but should an insoluble residue be left, this is to be tested for strychnine, brucine, and veratrine, according to the directions of 3.

b. A PRECIPITATE IS FORMED. The fluid is filtered off from the precipitate, and the filtrate subsequently treated as directed at § 141. 2. *a.* The precipitate is washed with cold water and subsequently dissolved in a little hydrochloric acid ; ammonia in excess is added to the solution and subsequently a sufficient quantity of ether.

α. *The precipitate which forms at first upon the addition of the ammonia, redissolves completely in the ether, and the clear fluid presents two distinct layers :* Absence of cinchonine ; presence of quinine or narcotine. The individual detection (and respective separation) of these two substances is then effected as directed at § 140. 2. *b.* α.

β. *The precipitate produced by the ammonia does not redissolve in the ether, or at least not completely :* CINCHONINE. Quinine or narcotine may also be present. The fluid is filtered off from the undissolved precipitate, and the filtrate tested for quinine and narcotine, as at α. The precipitate consists of cinchonine. To set all doubt on this point at rest, the precipitate is cautiously heated, when the exhalation of a peculiar aromatic odor will demonstrate the presence of cinchonine. Compare § 136. *c.* 3.)

3. The insoluble residue remaining upon the evaporation of the

solution of 2 *a.*, or of the filtrate of 2. *b.* is dried in the water bath and subsequently digested with absolute alcohol.

a. IT DISSOLVES COMPLETELY: Absence of strychnine; presence of brucine or veratrine. The alcoholic solution is evaporated to dryness, in the water bath, the residue divided into two portions, and the one subsequently tested for BRUCINE, with nitric acid and protochloride of tin, (§ 137. *b.* 6.), the other for VERATRINE, by means of concentrated sulphuric acid, (§ 137. *c.* 6.)

b. It does not dissolve, or at least not completely: STRYCHNINE. Brucine, and veratrine may likewise be present. The fluid is filtered off from the undissolved residue, and the filtrate subsequently examined for BRUCINE and VERATRINE according to the directions of § 141. 3. *a.* The identity of the precipitate with strychnine is demonstrated by the reaction with sulphuric acid containing nitric acid in admixture, and peroxide of lead, (§ 137. *a.* 8.)

4. A portion of the original solution is mixed with hydrochloric acid, the mixture heated to boiling and kept some time in ebullition. The formation of a precipitate demonstrates the presence of SALICINE. To set all doubt on this point at rest, the original substance is tested with concentrated sulphuric acid, (§ 138. 3.)

DETECTION OF THE VEGETO-ALKALIES IN PRESENCE OF COLORING AND EXTRACTIVE VEGETABLE OR ANIMAL MATTERS.

§ 142.

The presence of mucilaginous, extractive and coloring matters renders the detection of the vegeto-alkalies a task of considerable difficulty. These matters obscure the reactions so much that we are even unable to determine by a preliminary experiment, whether the substance under examination contains one of the vegeto-alkalies we have treated of in the foregoing paragraphs, or not. The most appropriate method of preparing substances containing these extraneous matters in admixture, for subsequent analysis in the usual way, is that recommended by MERCK, which I will give here with a few modifications:

The substance under examination is mixed with concentrated acetic acid to strongly acid reaction, and the mixture digested for several hours. The fluid is strained off from the solid part, and the latter is then washed with water acidified with acetic acid. The whole of the fluid obtained is evaporated to dryness in the water bath. The residue is boiled first with pure spirits of wine and subsequently with spirits of wine containing an admixture of acetic acid; the whole of the solution thus obtained is evaporated nearly to dryness in the water bath, again diluted with water, carbonate of potass added to feebly alkaline reaction, the mixture evaporated to syrupy consistence, and subsequently allowed to stand at rest for twenty-four hours; it is then again diluted with water, and the fluid is filtered off from the precipitate which has been formed in the process; the precipitate is washed with water, and subsequently digested with concentrated acetic acid; the solution obtained is diluted with water, decolorated with pure animal charcoal, and is then finally examined in the usual way for the vegeto-alkalies and for salicine.

II.

GENERAL PLAN OF THE ORDER AND SUCCESSION IN WHICH SUBSTANCES OUGHT TO BE ANALYSED FOR PRACTICE.

It is not a matter of indifference whether the student, in analysing for the sake of practice, follow no rule or order whatever in the selection of the substances which he intends to analyze, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways indeed may lead to the desired end, but one of them will invariably prove the shortest. I will therefore here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

Let the student take one hundred compounds, arranged in systematic order, (vide infra,) and let him analyze these compounds successively in the order in which they stand arranged. A careful and diligent examination of these will be amply sufficient to impart to him the necessary degree of skill in practical analysis. When analysing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed by a friend who knows their exact composition.

A. *From* 1 *to* 20.

Aqueous solutions of simple salts: e. g. sulphate of soda, nitrate of lime, chloride of copper, &c. These investigations will serve to teach the student the method of analysing substances soluble in water, containing but one base. In these investigations it is only intended to ascertain which base is present in the fluid under examination; but neither the detection of the acid, nor the proof of the absence of all other bases besides the one detected, are required.

B. *From* 21 *to* 50.

SALTS, &c., CONTAINING ONE BASE AND ONE ACID (in solid form, as powder): e. g. carbonate of barytes, borate of soda, phosphate of lime, arsenious acid, chloride of sodium, acetate of copper, sulphate of barytes, chloride of lead, &c. These investigations will serve to teach the student the method of effecting the solution of substances, and of detecting *one* acid and *one* metallic oxide, even though the substance under examination be insoluble in water. The detection of both the base and acid is required, but it is not necessary to prove that no other constituents are present.

C. *From* 51 *to* 70.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL BASES. These investigations will serve to teach the student the method of separating and distinguishing several metallic oxides from one another. The proof is required that no other bases are present besides those detected. No regard is paid to the acids.

I. From 51 to 60. These are intended to teach the student the method of separating the metallic oxides into the principal groups. The solutions contain, consequently, e. g. potass, lime, and lead; copper, iron, and arsenic; barytes, antimony, bismuth, and potass, &c.

II. 61 to 70. These are intended to teach the student the method of effecting the individual and separate detection of several bases belonging to one and the same group, and present conjointly in the same solution. The solutions contain, accordingly, e. g. potass, soda, and ammonia; zinc, manganese, and nickel; copper, mercury, and lead; antimony, tin, arsenic, &c.

D. *From* 71 *to* 80.

AQUEOUS SOLUTIONS CONTAINING SEVERAL ACIDS EITHER IN THE FREE STATE OR IN COMBINATION WITH BASES, e. g. sulphuric acid, phosphoric acid, and boracic acid;—carbonic acid, sulphuretted hydrogen, and hydrocyanic acid; tartaric acid, citric acid, and malic acid; chlorine, iodine, and bromine; nitric acid, hydrochloric acid, and oxalic acid. These investigations are intended to teach the student the method of detecting the several acids present conjointly in the same solution. The proof is required that no other acids are present besides those detected. The bases are disregarded.

E. *From* 81 *to* 100.

ALLOYS, MINERALS, AND MIXTURES OF EVERY DESCRIPTION;—the investigations will serve for further practice, and to prove that the student has attained a certain degree of practical skill in qualitative analysis. All the constituents of the substance under examination must be detected, and the nature of the substance ascertained.

III.

ARRANGEMENT OF THE RESULTS OF THE ANALYSES PERFORMED FOR PRACTICE.

The manner in which the results of analytical investigations ought to be noted and arranged is not a matter of indifference, as long as the student analyzes for practice.. The following examples will serve to illustrate the method which I have found the most appropriate in this respect.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS.

Nos. 1 *to* 20.

Colorless fluid of neutral reaction.

ClH	HS	NH_4S, HS	NH_4O, CO_2 and NH_4Cl
no precipitate, consequently no AgO Hg_2O	*no precipitate,* no PbO ,, HgO ,, CuO ,, BiO ,, CdO	*no precipitate,* no FeO ,, MnO ,, NiO ,, CoO ,, ZnO	*a white precipitate,* consequently either BaO, SrO, or CaO, no precipitate by solution of gypsum, consequently LIME. Confirmation by means of $\bar{O}$
	,, AsO_3 ,, AsO_5 ,, SbO_3 ,, SnO_2 ,, SnO ,, AuO_3 ,, PtO_2	,, Al_2O_3 ,, Cr_2O_3	
	,, Fe_2O_3		

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS

Nos. 21—50.

White powder melting in the crystallization water upon application of heat, and remaining subsequently unaltered—soluble in water—reaction neutral.

ClH	HS	NH_4S, HS	NH_4O, CO_2 NH_4, Cl	2 NaO,PO_5, and NH_3
no precipitate.	*no precipitate.*	*no precipitate.*	*no precipitate.*	*a white precipitate,* consequently MAGNESIA.

The detected base being MgO, and the analyzed substance being soluble in water, Cl, I, Br, SO_3 NO_5, $\bar{A}$, &c., are the only acids or metalloids that can be present. The absence of the organic acids and of nitric acid has been proved already by the preliminary examination.

$BaCl$ produces a white precipitate which ClH fails to dissolve; consequently SULPHURIC ACID.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 51—100.

A white powder, acquiring a permanent yellow tint upon application of heat. Before the blow-pipe, a ductile metallic grain, and yellow incrustation with white border upon cooling. Insoluble in water, effervescing with hydrochloric acid, incompletely soluble in this acid, readily soluble in nitric acid.

<table>
<tr><th rowspan="2">Cl H</th><th rowspan="2">HS</th><th colspan="2">NH_4 S, HS'</th><th rowspan="2">NH_4 O, CO_2</th><th rowspan="2"></th><th rowspan="2"></th></tr>
<tr><td colspan="2">White precipitate; solution of this in hydrochloric acid remains clear upon addition of potass in excess.</td></tr>
<tr><td rowspan="2">White precipitate insoluble in an excess of the precipitant, unaltered by ammonia: LEAD — confirmation by means of SO_3.</td><td rowspan="2">Black precipitate, insoluble in hydrosulphuret of ammonia, readily soluble in nitric acid. Examination for Cu, Bi, and Cd, results negative.</td><td>NH_4 Cl</td><td>HS</td><td rowspan="2">white precipitate; upon dissolving this in hydrochloric acid and adding subsequently solution of gypsum to the fluid, after some time a white precipitate forms: STRONTIA. Precipitation with sulphate of potass, filtrate tested for lime, with $\bar{O}$— results negative.</td><td rowspan="2">A fixed residue upon evaporation.</td><td rowspan="2">Hydrate of lime failed to evolve ammonia.</td></tr>
<tr><td>no precipitate.</td><td>white precipitate: ZINC.</td></tr>
</table>

Of the acids, carbonic acid has already been found. Of the remaining acids, the following cannot be present.

Organic acids: the preliminary examination has already proved their absence.

Nitric acid and chloric acid, because the analyzed substance is insoluble in water.

SH, Cl H, IH, Br H, because the analyzed substance was readily soluble in nitric acid.

Chromic acid: the white color of the analyzed compound proves the absence of this acid.

PO_5, BO_3, $\bar{O}$ might be present.

Examinations for these three acids yielded negative results.

IV.

TABLE

OF THE

MORE FREQUENTLY OCCURRING FORMS AND

COMPOUNDS OF THE SUBSTANCES TREATED OF IN THE

PRESENT WORK,

ARRANGED

WITH ESPECIAL REGARD TO THE CLASS, TO WHICH THEY RESPECTIVELY BELONG ACCORDING TO THEIR SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, OR IN NITRIC ACID.

PRELIMINARY REMARKS.

THE class to which the several compounds respectively belong according to the division specified at § 109, is expressed by figures. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, or nitric acid; 3 or III a substance insoluble both in water and acids. For those substances which stand as it were, on the limits between the various classes, the figures of the classes in question are jointly expressed: thus 1—2 signifies a substance difficultly soluble in water, but soluble in hydrochloric acid or nitric acid; 1—3 a body difficultly soluble in water and of which the solubility is not increased by the addition of the acids; and 2—3 a substance insoluble in water and difficultly soluble in hydrochloric acid and in nitric acid. Wherever the deportment of a substance with hydrochloric acid differs materially from that which it exhibits with nitric acid, this is stated in the notes.

The roman figures denote officinal and more commonly occurring compounds.

The haloid salts and sulphur compounds are placed in the corresponding column of the protoxide or of the peroxide. Most of the salts given are neutral, the basic and acid and double salts, if officinal, are mentioned in the notes; the small figures placed

A TABLE OF THE MORE COMMONLY OCCURRING

	KO	NaO	NH_4O	BaO	SrO	CaO	MgO	Al_2O_3	MnO	FeO	Fe_2O_3	CoO	NiO	ZnO
	I	I	I	I	1	I–II	II	II	II	II	II	II	II	II
S	I	I	I	I	I	I–II	2		II	II	II	$_{15}$	$_{16}$	II
Cl	I	I	I_{12}	I	I	I	1	1	I	I	I_{12}	I	I	1
J	I	1	1	1	1	1	1		1	1	1			1
SO_3	I_1	I	I_{13}	III	III	I–III	I	$I_{1\cdot13}$	I	I	I	1	1	I
NO_5	I	I	1	I	I	1	1	1	I	1	1	I		1
PO_5	1	I_{10}	1_{10}	2	2	II_{14}	2	2	2	2	II	2	2	2
CO_2	I_2	I_{11}	I	II	II	II	II		II	2		2		II
C_2O_3	I_3	1	I	2	2	II	2	2	2	1-2	1-2	2	2	2
BO_3	I_4	I_4	1	2	2	2	2	2	2	2	2	2	2	2
$\overline{A}$	I	I	I	I	1	1	1	1		1	I	1	1	I
$\overline{T}$	I_{4-9}	I_7	1_6	2	2	II	1-2	1	1-2	1-2	I_8	1		2
AsO_5	I	1	1	2	2	2	2	2	2	2	2	2	2	3
AsO_3	I	1	1	2	1	2				2		2	2	
CrO_3	I	1	1	2	2	1	1	2	1		1	2	1	

NOTES

1. Sulphate of potass and alumina I.
2. Bicarbonate of potass I.
3. Binoxalate of potass I.
4. Tartarized borax I.
5. Bitartrate of potash I.
6. Tartrate of potass and ammonia I.

near the corresponding neutral or simple salts, refer to these. Cyanogen, chloric acid, citric acid, malic acid, benzoic acid, succinic acid, and formic acid, are of more common occurrence in combination with a few bases only, and have therefore been omitted from the table. The most frequently occurring compounds of these substances are: cyanide of potassium I, ferrocyanide of potassium I, ferricyanide of potassium I, sesqui-ferrocyanide of iron (Prussian blue) III, ferrocyanide of zinc and potassium II—III, chlorate of potass I, the alkaline citrates I, the alkaline malates I, permalate of iron I, the alkaline benzoates I, the alkaline succinates I, and the alkaline formiates I.

FORMS AND COMBINATION OF BODIES.

	CdO	PbO	SnO	SnO_2	BiO_3	CuO	Hg_2O	HgO	AgO	PtO_2	AuO_3	SbO_3	Cr_2O_3
	2	II[18]	2	2 & 3	2	II[22]	II	II	2	2		[35]	II & III
S	2	2	[20]	[20]	2	[23]	III	III	[30]	[31]		II[36]	
Cl	1	I-III	I	1	I	I[24]	II-III	I[28]	III	I[32·33]	I[34]	I[37]	I
J	1	II	2	1			II	II	3				
SO_3	I	II-III	1		1	I[25]	1-2	I[29]	I-III	1		2	I
NO_5	1	I			I[21]	I	I[27]	I	1	1			I
PO_5	2	2				2	2	2	2				2
CO_2	2	II			2	II	2	2	2				
C_2O_3	2	II	2		2	2	2	2	2			1-2	1
BO_3	1-2	2	2		2	2	1		2				2
$\bar{A}$	1	I[19]	1	1	1	1[26]	1-2	1	1			1	1
$\bar{T}$	1-2	2	1-2		2	1	1-2	2	2			I[38]	1
AsO_5		2			2	2	2	2	2			2	1
AsO_3		2				II	2	2	2			2	
CrO_3		II-III	2		2	2	2	1-2	2			2	2

7. Tartrate of potass and soda I.
8. Tartrate of potass and peroxide of iron I.
9. Tartrate of antimony and potass I.
10. Phosphate of soda and ammonia I.
11. Bicarbonate of soda I.
12. Chloride of iron and ammonium I.
13. Sulphate of alumina and ammonia I.

14. Basic phosphate of lime II.
15. Sulphuret of cobalt is readily decomposed by nitric acid, but very difficultly by hydrochloric acid. This substance is not officinal.
16. The same applies to sulphuret of nickel.
17. Sulphuret of zinc. Readily soluble in nitric acid, somewhat difficultly soluble in hydrochloric acid.
18. Minium is converted by hydrochloric acid into chloride of lead, by nitric acid into oxide which redissolves in an excess of the acid, and into brown peroxide of lead, which is insoluble in nitric acid.
19. Triacetate of lead I.
20. Sulphuret and bisulphuret of tin are decomposed and dissolved by hydrochloric acid; by nitric acid they are converted into peroxide, which is insoluble in an excess of the acid. Sublimed bisulphuret of tin dissolves only in aqua regia.
21. Basic nitrate of bismuth II.
22. Ammoniacal oxide of copper 1.
23. Sulphuret of copper is difficultly decomposed by hydrochloric acid, but with facility by nitric acid.
24. Chloride of copper and ammonium 1.
25. Sulphate of copper and ammonia 1.
26. Basic acetate of copper, soluble partially in water, and completely in acids.
27. Basic nitrate of protoxide of mercury and ammonia II.
28. Basic chloride of mercury and ammonium II.
29. Basic sulphate of peroxide of mercury II.
30. Sulphuret of silver soluble only in nitric acid.
31. Sulphuret of platinum is not effected by hydrochloric acid; boiling nitric acid converts it into a soluble sulphate of peroxide of platinum.
32. Chloride of platinum and potassium 1—3.
33. Chloride of platinum and ammonium 1—3.
34. Chloride of gold and sodium I.

35. Oxide of antimony soluble in hydrochloric acid, but not in nitric acid.
36. Sulphuret of antimony and calcium 1—2.
37. Basic chloride of antimony II.
38. Tartrate of antimony and potass I.

THE END.

LONDON:
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ERRATA.

Page 34, last line in note, *leave out* acid.
237, — 19. *for* 101. c. *read* 101 e.
305, line seven from bottom, *leave out* or.

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